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L7: Entry 21 of 38 File: USPT Mar 16, 1999

US-PAT-NO: 5882662
DOCUMENT-IDENTIFIER: US 5882662 A

TITLE: Cosmetic compositions containing smectite gels

DATE-ISSUED: March 16, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Pahlck; Harold E.	Waldwick	NJ		
Fleissman; Leona Giat	Ridgewood	NJ		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
Avon Products, Inc.	New York	NY			02

APPL-NO: 08/ 853992 [PALM]
DATE FILED: May 9, 1997

INT-CL: [06] A61 K 7/00

US-CL-ISSUED: 424/401; 424/DIG.5, 514/944
US-CL-CURRENT: 424/401; 424/DIG.5, 514/944

FIELD-OF-SEARCH: 424/401, 424/DIG.5, 514/770, 514/944

PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

Search Selected | Search ALL

	PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
☐	3855147	December 1974	Granquist	252/317
☐	4040974	August 1977	Wright et al.	252/316
☐	4116866	September 1978	Finlayson	252/316
☐	4275222	June 1981	Scala, Jr.	560/103
☐	4425244	January 1984	House	252/28
☐	4462981	July 1984	Smith	424/27
☐	4550035	October 1985	Smith	427/398.1
☐	4637933	January 1987	Arriban et al.	424/131
☐	4659571	April 1987	Laba	424/65
☐	4894182	January 1990	Cody et al.	252/315.2
☐	4929644	May 1990	Guilbeaux	514/642
☐	5015469	May 1991	Yoneyama et al.	424/59
☐	5165915	November 1992	Tokubo et al.	424/63
☐	5336647	August 1994	Nae et al.	501/146
☐	5356617	October 1994	Schlossman	424/63
☐	5376604	December 1994	Iwasaki et al.	501/146
☐	5429999	July 1995	Nae et al.	501/146
☐	5478552	December 1995	Hasegawa	424/63
☐	5487840	January 1996	Yabe et al.	252/62.51

ART-UNIT: 165

PRIMARY-EXAMINER: Page; Thurman K.

ASSISTANT-EXAMINER: Spear; James M.

ATTY-AGENT-FIRM: Ohlandt, Greeley, Ruggiero & Perle

ABSTRACT:

A cosmetic composition comprising a smectite clay and a lipophilic polar solvent. The smectite clay gels the polar solvent without addition of a polar activator. A method for the preparation of a smectite clay gel is also revealed.

25 Claims, 0 Drawing figures
Exemplary Claim Number: 1

BRIEF SUMMARY:

1 The present invention relates generally to cosmetic compositions containing smectite clay gels. More particularly, this invention relates to a cosmetic composition containing a synthetic smectite clay gelled with a polar solvent. The resulting composition or gel is used to bind and give structure to cosmetic compositions.

2 BACKGROUND OF THE INVENTION

3 Various binding and structuring agents are known for use in cosmetic compositions, such as lipsticks and eyeshadows. Traditionally, organic and inorganic waxes are used as binding and structuring agents in such compositions. However, many

consumers dislike the inherently waxy feel and build-up of such wax-based cosmetics. Accordingly, a demand exists for non-wax binding and structuring agents.

4 A number of water-based gellants are in use in the cosmetic art as binding and structuring agents. These water-based gellants are primarily thickening agents, such as gums, added in limited amounts to aqueous carrier solutions. However, these thickening agents have limitations. For example, they must be incorporated into the composition under high temperature and high shear. In addition, clay based products such as the Bentone gels are also known for use as binding and structuring agents. These clay powders form gels in various oils. However, high shear must be applied to these clay-based gels during formulation, and separate polar activating agents such as propylene carbonate and other short chain polar compounds must be added to form the gels. Other clays, such as certain modified organophilic clays, are known to swell in and gel organic liquids without the addition of polar dispersion additives. However, these systems typically use such solvents as short chain alcohols, ketones or toluene, and require high energy shear to permit the gel to form.

5 Accordingly, there is a need for a cosmetic gel that can be used as a carrier to bind and give structure to the cosmetic composition, and that can replace part or all of the wax content of traditional cosmetic formulations.

6 SUMMARY OF THE INVENTION

7 Against the foregoing background, it is a primary object of the present invention to provide a cosmetic composition having a gelled carrier that is substantially wax-free or has a lower wax content than traditional cosmetics.

8 It is another object of the present invention to provide a cosmetic composition that can be formulated at low temperature and with the application of minimal shear.

9 It is yet another object of the present invention to provide a cosmetic composition that can be formulated as a liquid, poured or injected into a holder and subsequently heat set, to facilitate the packaging process.

10 To the accomplishment of the foregoing objects and advantages, the present invention, in brief summary, is a cosmetic composition comprising a smectite clay and a lipophilic polar solvent. The smectite clay gels the polar solvent without addition of a polar activator. A method for the preparation of a smectite clay gel is also revealed.

DETAILED DESCRIPTION:

1 DESCRIPTION OF THE PREFERRED EMBODIMENTS

2 The present invention provides a unique cosmetic gel base comprising a clay, preferably a smectite clay, and a hydrocarbon-based lipophilic polar solvent. This cosmetic gel base is preferably a gel cosmetic, into which cosmetic agents such as colorants, emollients, and healing or treatment agents can be incorporated for delivery to the skin. Use of this cosmetic gel base allows the formation of a stick or cake cosmetic while eliminating or reducing the need for waxes or gums to bind or thicken the cosmetic composition. Finished products can also include soft gels and emulsions. In alternate embodiments, liquid and gel compositions can also be thickened with the gel of this invention. The smectite clay gel can act to improve yield value, or suspension of solids, within a liquid.

3 The preferred clay of the present invention is a smectite clay. More preferably, the clay is a synthetic smectite clay. Synthetic smectite clays are advantageous because they typically have a lower impurity content. However, any clay that has been cleaned to remove impurities can be used in the present invention.

4 The most preferred clay of the present invention is a synthetic smectite SAN clay distributed by Kobo Products Inc. and manufactured by Nikko Chemicals Co., Ltd. Kobo has disclosed the structure of its synthetic smectite clay, called lucentite SAN, as including 60.00 to 70.00 percent lithium magnesium sodium silicate (Na.sub.0-0.33 (Mg.sub.2.67 Li.sub.0.33) (Si.sub.4 O.sub.4) (OH).sub.2) and 30.00 to 40.00 percent quaternium -18 ([R.sub.2 N(CH.sub.3).sub.2], where R is C.sub.16 .about.C.sub.18). Kobo has also stated that guaternium-18 is not reacted with lithium magnesium sodium silicate to form the lucentite SAN.

5 The present invention discloses the use of smectite SAN clay, swelled with a polar lipophilic hydrocarbon-based solvent, as a gel base or pomade for a cosmetic product. The cosmetic is preferably pigmented, but need not be. A pumpable product is produced that will set up once poured or injected into a mold. Moreover, the gelling agent/cosmetic base is chilled during formulation and is subsequently heat set to form a solidified product. This is contrary to typical cosmetic formulation practice in which the components are heated during mixing and the finished product is then cooled to set.

6 Gel stability is related to solvent polarity, with more highly polar solvents forming more stable gels. The smectite clay is preferably gelled with a polar lipophilic hydrocarbon-based solvent, more preferably a C.sub.6 or higher polar solvent. The most preferred solvents are benzoate esters, such as C.sub.12-15 alcohols benzoate (Finsolv TN), and salicylate esters. However, the solvent C.sub.12-15 alcohol lactate is also preferred, since it also swells the synthetic smectite effectively.

7 The gelled smectite clay permits the formation of stick, cake or other solid or semi-solid cosmetics having no or limited wax content. The smectite clay gels provide stick integrity and lattice strength without the use of waxes. Moreover, liquid or other non-solid compositions can also be thickened with the gels of the present invention.

8 The smectite clay can be gelled with non-volatile lipophilic solvents. Of the non-volatile lipophilic solvents, organic solvents are preferred. Of these organic solvents, aromatic compounds are preferred, with esters being most preferred.

9 By varying the concentration of the smectite clay, a variety of product forms can result. For example, a liquid is formed at lower clay concentrations. At intermediate concentrations, a hot pour consistency is achieved. At higher concentrations, pomades and sticks can be formed.

10 These smectite clay gels have been found to have unique aesthetics. For example, when heat is applied to the clay/solvent mixture, the clay sets up instantaneously, forming a "standing wave." The stable gel that is created becomes sufficiently stiff to form peaks that do not flow back to their original position, so that the finished product has a smooth and creamy consistency. This unexpected result permits the gel that is formed to be used as a structural agent, and not just as a thickener. Depending on the content of pigments and powders, the finished product can also have a smooth powdery feel. Moreover, the gel and compositions containing the gel do not need to be compressed to form a cake or stick. Also, the finished product has an improved stability over time and over a wide range of temperatures. In addition, clearer, truer colors can be provided using the gel base of the present invention. Furthermore, the gel formed is unexpectedly clear or translucent, providing more versatility to the cosmetics formulator, including the option of producing clear or translucent finished products. Such clear products can be formulated, for example, when the smectite clays are cold mixed into organic oils containing aromatic ring structures, and the mixture is then heated. Furthermore, the finished product has good payoff, a smooth and creamy feel on application, and even delivery to the skin.

11 As discussed, the smectite gels of the present invention do not require high shear. Clay gels known in the art, such as Bentone gels, require the application of high shear to form the gels. Such high shear necessitates the addition of large quantities of mechanical energy to the system, as in a commercial homogenizer. On the other hand, the smectite gels of the present invention can be mixed by hand

with a spatula, or with the commercial equivalent thereof. Sufficient force to thoroughly incorporate the pigments and other components into the solvent is required, but the use of high shear, as required by prior art clay gels, is not necessary.

12 Concerning the clear or translucent property of the finished product, the most preferred solvents, benzoate esters, form transparent gels when combined with the smectite clay and swelled with the application of heat. Finsolv TN (C.sub.12 -C.sub.15 alcohols benzoate) is the most preferred ester for use in the compositions of the present invention. Pure C.sub.12 and C.sub.18 alcohols benzoate performed equivalently. When the smectite clay, preferably smectite SAN, is combined with octyl salicylate, a totally clear gel is formed. However, the gel strength is less than that of the Finsolv TN gel. This salicylate composition, after heating, reflects purple UV light. It appears that the smectite SAN solubilizes or disperses into this salicylate ester to provide the clear gel. Guerbet alcohols such as butyl octyl salicylate, butyl octyl benzoate and hexyl decyl benzoate also perform well as solvents.

13 Other preferred solvents include C.sub.12 -C.sub.15 alcohol lactate (Ceraphyl 41 from ISP) and C.sub.12 -C.sub.15 alcohol octanoate. Still other preferred solvents include phenyl trimethicone, Finsolv SB, Finsolv BOD, Finsolv PG-22, Surfadone LP300, Finsolv 116, Finsolv 137, Finsolv EMG20, alkyl 12-15 salicylate, tridecyl salicylate, isocetyl salicylate, laureth 2-benzoate, and phenylethylmethyl polydimethylsiloxane. Any aliphatic or aromatic polar solvent, organosilicone, ester, or compound or derivative thereof, can be used in the present invention.

14 Compositions of the present invention are also beneficial because they have superior high temperature stability. For example, they will not melt readily in hot climates or in hot car trunks. Furthermore, these compositions can be formulated to be wax free, and are resistant to or free of syneresis.

15 A preferred composition according to the present invention is formulated by the following steps:

16 1) mixing with minimal shear the synthetic smectite and the solvent at ambient to cold temperatures;

17 2) dispensing the mixture into a pan or other container;

18 3) applying heat to the mixture to swell and set the gel base.

19 The heat can be applied by radial, convectional, mechanical or electrical energy or by a combination thereof.

20 In the absence of other ingredients, it is preferred that the smectite clay be combined with the preferred Finsolv TN polar solvent at about 15% to about 85% by weight of the total weight of the composition. For example, a preferred two component stick can be made of about 20% by weight smectite clay and 80% by weight of Finsolv TN. A preferred multi-component pomade can be made of about 20% by weight smectite clay, about 20% by weight Finsolv TN, and about 60% adjunct ingredients such as pigments, film formers and preservatives. It is more preferred that the Finsolv TN be present at more than about 20% by weight of the total composition. However, the preferred amount of Finsolv TN can be varied depending on the effect other ingredients have on polarity. For example, phenyl trimethicone augments the polarity of the solvent, and accordingly less solvent is needed. Moreover, when other solvents are used in addition to or instead of Finsolv TN, the preferred amount will vary.

21 The resulting gel can be present at any weight percent of the total composition, depending on the desired function.

22 A preferred eyeshadow according to the present invention follows:

	Wt. %
Part A	15
Smectite SAN	
Part B - Oil phase	
Finsolv TN	35
Phenyl trimethicone	3.7
Film formers	12.3
Part C - Powders, etc.	
Pearls and pigments	22
Powders	11.5
Methyl paraben	0.3
Propyl paraben	0.2

23 In this preferred eyeshadow composition, it is most preferred that the powders contain a high concentration of platelet powders in relation to the concentration of particulate powders, to provide the desired cosmetic effect.

24 The foregoing composition was formulated according to the following procedure:

25 1. The oil phase ingredients were mixed.

26 2. The oil phase is placed in an ice bath or other cool environment at approximately 40.degree. F.

27 3. After the oil phase has chilled, the smectite SAN is added.

28 4. The mixture is mixed until homogeneous, while maintaining the temperature.

29 5. The remaining ingredients are added and the mixture is mixed until homogeneous, maintained at 40.degree. F. to 50.degree. F.

30 6. The mixture is kept cool, preferably by storing in a refrigerator or freezer, until the batch is ready to be processed.

31 The batch is then packaged using the back injection molding process according to the following steps:

32 7. The batch or batches to be processed are placed into an ice bath.

33 8. Hoses conducting product from the back injection equipment are placed into the product containers.

34 9. The back injection process is run as usual, except there is no need for a vacuum to remove alcohol or other volatile components from the batch.

35 10. The filled pans are removed from the die and can be stored until needed.

36 11. The pan containing the product is heated to induce swelling of the smectite. The lattice of the gel is thus activated and the product is set and ready for use once the pan has cooled to ambient temperature.

37 The cosmetic compositions of the present invention are particularly suited for use with back injection equipment and process. This back injection process is commonly used in packaging cosmetic formulations. In this process, a solvent-based slurry of the cosmetic composition is injected through an aperture in the back, or base, of a cosmetic pan. The slurry then cools and solidifies in the pan to form the finished product. The cosmetic compositions of the present invention, however, can be slurried and injected at cool, ambient or heated temperature. They are pumpable when mechanical energy is applied, and set up when at rest. Thus, it is preferred

to pump the product in a cool state (about 40.degree. C. to about 50.degree. C.) to prevent swelling until the product is in the final container. Moreover, no volatile solvent base is necessary. This, in turn, eliminates the need to evaporate off the alcohol or other volatile solvent.

38 The back injection molding process utilizes pans having holes through which the product is pumped. Each pan may have multiple holes, enabling more than one shade or product type to be filled into each pan without the need for double processing. Embossing and debossing is also feasible, to form raised or sunken surfaces on the finished product. This permits the creation of a wide variety of cosmetic effects. Dwell times, pressures and the use of a vacuum can affect the aesthetics of the surface of the finished product, and should be optimized for each formulation. The smectite clays of the present invention can be gelled and combined with a compatible volatile solvent, such as a polar volatile solvent, to provide a long-wearing product, which preferably also contains a cosmetic film former component. Additionally, the product can be swelled and set with the careful application of heat, making the process easier to control. The application of heat must be controlled (for example, the product can be heated in a closed container) to prevent evaporation of the volatile solvent when the volatile solvent is an integral part of the finished composition.

39 The invention having been thus described with particular reference to the preferred forms thereof, it will be obvious that various changes and modifications may be made therein without departing from the spirit and scope of the invention as defined in the appended claims.

CLAIMS:

What we claim is:

1. A cosmetic composition comprising a smectite clay and a lipophilic polar solvent, wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear.

2. The cosmetic composition of claim 1, wherein said smectite clay is synthetic.

3. A cosmetic composition comprising a smectite clay and a lipophilic polar solvent, wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear, and wherein said smectite clay is synthetic lucentite SAN.

4. A cosmetic composition comprising a smectite clay and a lipophilic polar solvent, wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear, and wherein said smectite clay includes lithium magnesium sodium silicate and quaternium-18.

5. The cosmetic composition of claim 4, wherein said lithium magnesium sodium silicate is present at about 60 to about 70 weight percent of the smectite clay, and said quaternium-18 is present at about 30 to about 40 weight percent of the smectite clay.

6. A cosmetic composition comprising:

a smectite clay; and

a lipophilic polar solvent selected from the group consisting of benzoate esters, salicylate esters, Guerbet alcohols, C.sub.12 -C.sub.15 alcohol lactate, C.sub.12 -C.sub.15 alcohol octanoate, phenyl trimethicone, Surfadone LP300, and phenylethylmethyl polydimethylsiloxane;

wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear.

7. The cosmetic composition of claim 1, wherein said polar solvent is aromatic.

8. A method of forming a cosmetic composition, comprising:

(a) mixing a smectite clay with a lipophilic polar solvent at a temperature of no more than about 40.degree. F. to about 50.degree. F. to form a clay/solvent mixture; and

(b) heating said clay/solvent mixture to form a swelled gel.

9. A cosmetic composition comprising a smectite clay and a lipophilic polar solvent, wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear, and wherein said polar solvent is selected from the group consisting of benzoate esters, salicylate esters, C.sub.12 -C.sub.15 alcohol lactate, and a combination thereof.

10. A cosmetic composition comprising a smectite clay and a lipophilic polar solvent, wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear, and wherein said composition is in a form selected from the group consisting of stick form and cake form.

11. The method of claim 8, wherein said composition is substantially clear.

12. A cosmetic composition comprising a smectite clay and a lipophilic polar solvent, wherein said smectite clay gels said polar solvent without addition of a polar activator and without high shear, and wherein said composition is substantially clear.

13. The cosmetic composition of claim 1, wherein said composition is translucent.

14. The method of of claim 8, wherein said composition is translucent.

15. The method of claim 8, wherein said clay/solvent mixture is kept cool before being heated.

16. The method of claim 8, further comprising a step of transferring said clay/solvent mixture into at least one cosmetic container, and wherein said clay/solvent mixture is heated in said at least one cosmetic container.

17. The method of claim 16, wherein said clay/solvent mixture is transferred into said at least one cosmetic container by a back injection process.

18. The method of claim 8, wherein said smectite clay is synthetic.

19. The method of claim 8, wherein said smectite clay is synthetic lucentite SAN.

20. The method of claim 8, wherein said smectite clay includes lithium magnesium sodium silicate and quaternium-18.

21. The method of claim 20, wherein said lithium magnesium sodium silicate is present at about 60 to about 70 weight percent of the smectite clay, and said quaternium-18 is present at about 30 to about 40 weight percent of the smectite clay.

22. The method of claim 8, wherein said polar solvent is organic.

23. The method of claim 22, wherein said polar solvent is selected from the group consisting of aromatic compounds, esters, silicones, and a combination thereof.

24. The method of claim 8, wherein said polar solvent is selected from the group consisting of benzoate esters, salicylate esters, C.sub.12 -C.sub.15 alcohol lactate, and a combination thereof.

25. The cosmetic composition of claim 1, wherein said polar solvent is C.sub.6 or higher.

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US Pre-Grant Publication Full-Text Database
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IBM Technical Disclosure Bulletins

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	DB=USPT,PGPB,JPAB,EPAB,DWPI; PLUR=YES; OP=OR		
L7	L6 and (solvent)same(water)	38	L7
L6	(wax) and (smectite)adj1(clay)same(solvent)	43	L6
L5	(expandible)adj1(clay)same(smectite)	2	L5
L4	L3 and (solvent)same(water)	54	L4
L3	l1 and (smectite)adj1(clay)same(solvent)	76	L3
L2	L1 and (smectite)adj1(clay)	1419	L2
L1	powder	914410	L1

END OF SEARCH HISTORY

09/750,936

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☐ 1. Document ID: US 20030176537 A1

L7: Entry 1 of 38 File: PGPB Sep 18, 2003

PGPUB-DOCUMENT-NUMBER: 20030176537
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030176537 A1

TITLE: Composite materials with improved phyllosilicate dispersion

PUBLICATION-DATE: September 18, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Chaiko, David J.	Naperville	IL	US	

US-CL-CURRENT: 523/200; 524/445, 524/449, 524/451

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 2. Document ID: US 20030162877 A1

L7: Entry 2 of 38 File: PGPB Aug 28, 2003

PGPUB-DOCUMENT-NUMBER: 20030162877
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030162877 A1

TITLE: Process for the preparation of organoclays

PUBLICATION-DATE: August 28, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Chaiko, David J.	Napervill	IL	US	

US-CL-CURRENT: 524/445; 524/487

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 3. Document ID: US 20030152531 A1

L7: Entry 3 of 38 File: PGPB Aug 14, 2003

PGPUB-DOCUMENT-NUMBER: 20030152531
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030152531 A1

TITLE: Multifunctional particulate additive for personal care and cosmetic compositions, and the process of making the same

PUBLICATION-DATE: August 14, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
SenGupta, Ashoke K.	Barrington	IL	US	
Spindler, Ralph	Palatine	IL	US	
Darlington, Jerald W. JR.	Marengo	IL	US	

US-CL-CURRENT: 424/59; 424/60

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 4. Document ID: US 20020182155 A1

L7: Entry 4 of 38   File: PGPB   Dec 5, 2002

PGPUB-DOCUMENT-NUMBER: 20020182155
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020182155 A1

TITLE: Multifunctional particulate additive for personal care and cosmetic compositions, and the process of making the same

PUBLICATION-DATE: December 5, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
SenGupta, Ashoke K.	Barrington	IL	US	
Spindler, Ralph	Palatine	IL	US	
Darlington, Jerald W. JR.	Marengo	IL	US	

US-CL-CURRENT: 424/59; 424/400, 424/401, 424/60, 424/78.02, 424/78.08

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 5. Document ID: US 20020085983 A1

L7: Entry 5 of 38   File: PGPB   Jul 4, 2002

PGPUB-DOCUMENT-NUMBER: 20020085983
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020085983 A1

TITLE: Segmented composition and a method and a system for making same

PUBLICATION-DATE: July 4, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Fleissman, Leona G.	Ridgewood	NJ	US	
Santini, Anthony M.	Yonkers	NY	US	

US-CL-CURRENT: 424/64

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 6. Document ID: US 20010008633 A1

L7: Entry 6 of 38   File: PGPB   Jul 19, 2001

PGPUB-DOCUMENT-NUMBER: 20010008633
PGPUB-FILING-TYPE: new-utility
DOCUMENT-IDENTIFIER: US 20010008633 A1

TITLE: Cosmetic stick

PUBLICATION-DATE: July 19, 2001

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Travkina, Irina	River Edge	NJ	US	
Raouf, Maha	Franklin Lakes	NJ	US	
Pahlck, Harold	Waldwick	NJ	US	

US-CL-CURRENT: 424/401; 510/130

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 7. Document ID: US 6627598 B1

L7: Entry 7 of 38   File: USPT   Sep 30, 2003

US-PAT-NO: 6627598
DOCUMENT-IDENTIFIER: US 6627598 B1

TITLE: Solid detergent compositions comprising an organophilic smectite clay

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 8. Document ID: US 6500411 B2

L7: Entry 8 of 38   File: USPT   Dec 31, 2002

US-PAT-NO: 6500411
DOCUMENT-IDENTIFIER: US 6500411 B2

TITLE: Multifunctional particulate additive for personal care and cosmetic compositions, and the process of making the same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 9. Document ID: US 6461423 B1

L7: Entry 9 of 38   File: USPT   Oct 8, 2002

US-PAT-NO: 6461423

DOCUMENT-IDENTIFIER: US 6461423 B1
** See image for Certificate of Correction **

TITLE: Intercalates and exfoliates formed with hydroxyl-functional; polyhydroxyl-functional; and aromatic compounds; composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 10. Document ID: US 6365139 B2

L7: Entry 10 of 38 File: USPT Apr 2, 2002

US-PAT-NO: 6365139
DOCUMENT-IDENTIFIER: US 6365139 B2
** See image for Certificate of Correction **

TITLE: Cosmetic stick

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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Terms	Documents
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☐ 11. Document ID: US 6287634 B1

L7: Entry 11 of 38 File: USPT Sep 11, 2001

US-PAT-NO: 6287634
DOCUMENT-IDENTIFIER: US 6287634 B1

TITLE: Intercalates and exfoliates formed with monomeric ethers and esters; composite materials containing same methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 12. Document ID: US 6242500 B1

L7: Entry 12 of 38 File: USPT Jun 5, 2001

US-PAT-NO: 6242500
DOCUMENT-IDENTIFIER: US 6242500 B1
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with long chain (C6+) or aromatic matrix polymer-compatible monomeric, oligomeric or polymeric intercalant compounds, and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 13. Document ID: US 6183760 B1

L7: Entry 13 of 38 File: USPT Feb 6, 2001

US-PAT-NO: 6183760
DOCUMENT-IDENTIFIER: US 6183760 B1

TITLE: Cosmetic stick

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 14. Document ID: US 6126734 A

L7: Entry 14 of 38 File: USPT Oct 3, 2000

US-PAT-NO: 6126734
DOCUMENT-IDENTIFIER: US 6126734 A

TITLE: Intercalates and exfoliates formed with hydroxyl-functional; polyhydroxyl-functional; and aromatic compounds; composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 15. Document ID: US 6124365 A

L7: Entry 15 of 38 File: USPT Sep 26, 2000

US-PAT-NO: 6124365
DOCUMENT-IDENTIFIER: US 6124365 A

TITLE: Intercalates and exfoliates formed with long chain (C6+) or aromatic matrix polymer-compatible monomeric, oligomeric or polymeric intercalant compounds and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 16. Document ID: US 6103687 A

L7: Entry 16 of 38 File: USPT Aug 15, 2000

US-PAT-NO: 6103687
DOCUMENT-IDENTIFIER: US 6103687 A
**** See image for Certificate of Correction ****

TITLE: Non-volatile quaternary ammonium compositions and their uses

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 17. Document ID: US 6083559 A

L7: Entry 17 of 38 File: USPT Jul 4, 2000

US-PAT-NO: 6083559
DOCUMENT-IDENTIFIER: US 6083559 A

TITLE: Intercalates and exfoliates formed with hydroxyl-functional; polyhydroxyl-functional; and aromatic compounds; composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 18. Document ID: US 5998528 A

L7: Entry 18 of 38 File: USPT Dec 7, 1999

US-PAT-NO: 5998528
DOCUMENT-IDENTIFIER: US 5998528 A

TITLE: Viscous carrier compositions, including gels, formed with an organic liquid carrier, a layered material: polymer complex, and a di-, and/or tri-valent cation

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 19. Document ID: US 5952095 A

L7: Entry 19 of 38 File: USPT Sep 14, 1999

US-PAT-NO: 5952095
DOCUMENT-IDENTIFIER: US 5952095 A

TITLE: Intercalates and exfoliates formed with long chain (C.sub.10 +) monomeric organic intercalant compounds; and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 20. Document ID: US 5935272 A

L7: Entry 20 of 38 File: USPT Aug 10, 1999

US-PAT-NO: 5935272
DOCUMENT-IDENTIFIER: US 5935272 A

TITLE: Compositions comprising aryloxypolyoxyalkylene naphthalimide derivative colorants

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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Terms	Documents
L6 and (solvent)same(water)	38

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Search Results - Record(s) 21 through 30 of 38 returned.

☐ 21. Document ID: US 5882662 A

L7: Entry 21 of 38 File: USPT Mar 16, 1999

US-PAT-NO: 5882662
DOCUMENT-IDENTIFIER: US 5882662 A

TITLE: Cosmetic compositions containing smectite gels

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 22. Document ID: US 5880197 A

L7: Entry 22 of 38 File: USPT Mar 9, 1999

US-PAT-NO: 5880197
DOCUMENT-IDENTIFIER: US 5880197 A

TITLE: Intercalates and exfoliates formed with monomeric amines and amides: composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 23. Document ID: US 5877248 A

L7: Entry 23 of 38 File: USPT Mar 2, 1999

US-PAT-NO: 5877248
DOCUMENT-IDENTIFIER: US 5877248 A
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with oligomers and polymers and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 24. Document ID: US 5849830 A

L7: Entry 24 of 38 File: USPT Dec 15, 1998

US-PAT-NO: 5849830
DOCUMENT-IDENTIFIER: US 5849830 A
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with N-alkenyl amides and/or acrylate-functional pyrrolidone and allylic monomers, oligomers and copolymers and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 25. Document ID: US 5830528 A

L7: Entry 25 of 38 File: USPT Nov 3, 1998

US-PAT-NO: 5830528
DOCUMENT-IDENTIFIER: US 5830528 A
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with hydroxyl-functional; polyhydroxyl-functional; and aromatic compounds; composites materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 26. Document ID: US 5804613 A

L7: Entry 26 of 38 File: USPT Sep 8, 1998

US-PAT-NO: 5804613
DOCUMENT-IDENTIFIER: US 5804613 A
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with monomeric carbonyl-functional organic compounds, including carboxylic and polycarboxylic acids; aldehydes; and ketones; composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 27. Document ID: US 5780618 A

L7: Entry 27 of 38 File: USPT Jul 14, 1998

US-PAT-NO: 5780618
DOCUMENT-IDENTIFIER: US 5780618 A

TITLE: Oxidized cellulose

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 28. Document ID: US 5760121 A

L7: Entry 28 of 38 File: USPT Jun 2, 1998

US-PAT-NO: 5760121
DOCUMENT-IDENTIFIER: US 5760121 A

TITLE: Intercalates and exfoliates formed with oligomers and polymers and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 29. Document ID: US 5759938 A

L7: Entry 29 of 38 File: USPT Jun 2, 1998

US-PAT-NO: 5759938
DOCUMENT-IDENTIFIER: US 5759938 A

TITLE: Process for producing organoclays with quaternary ammonium compositions made using non volatile diluents

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 30. Document ID: US 5735943 A

L7: Entry 30 of 38 File: USPT Apr 7, 1998

US-PAT-NO: 5735943
DOCUMENT-IDENTIFIER: US 5735943 A
**** See image for Certificate of Correction ****

TITLE: Rheological additives for asphalt and other organic systems comprising one or more organoclays and fibrous material, a process for producing such additives and organic systems containing such additives

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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Terms	Documents
L6 and (solvent)same(water)	38

Display Format: - Change Format

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Search Results - Record(s) 31 through 38 of 38 returned.

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31. Document ID: US 5721306 A

L7: Entry 31 of 38 File: USPT Feb 24, 1998

US-PAT-NO: 5721306
DOCUMENT-IDENTIFIER: US 5721306 A

TITLE: Viscous carrier compositions, including gels, formed with an organic liquid carrier and a layered material:polymer complex

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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32. Document ID: US 5634969 A

L7: Entry 32 of 38 File: USPT Jun 3, 1997

US-PAT-NO: 5634969
DOCUMENT-IDENTIFIER: US 5634969 A

TITLE: Organoclay compositions

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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33. Document ID: US 5414079 A

L7: Entry 33 of 38 File: USPT May 9, 1995

US-PAT-NO: 5414079
DOCUMENT-IDENTIFIER: US 5414079 A

TITLE: Oxidized cellulose

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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34. Document ID: US 5114481 A

L7: Entry 34 of 38 File: USPT May 19, 1992

US-PAT-NO: 5114481
DOCUMENT-IDENTIFIER: US 5114481 A
**** See image for Certificate of Correction ****

TITLE: Aerosol-type, sprayable, water-in-liquid hydrocarbon multicolor paint and process for making

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 35. Document ID: US 4913828 A
L7: Entry 35 of 38 File: USPT Apr 3, 1990

US-PAT-NO: 4913828
DOCUMENT-IDENTIFIER: US 4913828 A

TITLE: Conditioning agents and compositions containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 36. Document ID: US 4536315 A
L7: Entry 36 of 38 File: USPT Aug 20, 1985

US-PAT-NO: 4536315
DOCUMENT-IDENTIFIER: US 4536315 A

TITLE: Perfume-containing carrier having surface-modified particles for laundry composition

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 37. Document ID: US 4193454 A
L7: Entry 37 of 38 File: USPT Mar 18, 1980

US-PAT-NO: 4193454
DOCUMENT-IDENTIFIER: US 4193454 A

TITLE: Super-active clay catalyst and use thereof

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 38. Document ID: US 3963852 A
L7: Entry 38 of 38 File: USPT Jun 15, 1976

US-PAT-NO: 3963852
DOCUMENT-IDENTIFIER: US 3963852 A

TITLE: Clay-coated record material of improved image durability

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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Terms	Documents
L6 and (solvent)same(water)	38

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Search Results -

Terms	Documents
(expandible)adj1(clay)same(smectite)	2

Database:
US Patents Full-Text Database
US Pre-Grant Publication Full-Text Database
JPO Abstracts Database
EPO Abstracts Database
Derwent World Patents Index
IBM Technical Disclosure Bulletins

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Recall Text | Clear

Search History

DATE: Monday, November 24, 2003 Printable Copy Create Case

Set Name side by side	Query	Hit Count	Set Name result set
	DB=USPT,PGPB,JPAB,EPAB,DWPI; PLUR=YES; OP=OR		
L5	(expandible)adj1(clay)same(smectite)	2	L5
L4	L3 and (solvent)same(water)	54	L4
L3	l1 and (smectite)adj1(clay)same(solvent)	76	L3
L2	L1 and (smectite)adj1(clay)	1419	L2
L1	powder	914410	L1

END OF SEARCH HISTORY

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Search Results - Record(s) 1 through 2 of 2 returned.

☐ 1. Document ID: US 4808251 A

L5: Entry 1 of 2 File: USPT Feb 28, 1989

US-PAT-NO: 4808251
DOCUMENT-IDENTIFIER: US 4808251 A

TITLE: Water-in-oil emulsion explosive compositions containing organophilic smectite clay

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw. Desc | Image

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☐ 2. Document ID: US 4740488 A

L5: Entry 2 of 2 File: USPT Apr 26, 1988

US-PAT-NO: 4740488
DOCUMENT-IDENTIFIER: US 4740488 A

TITLE: Modified clay sorbents

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw. Desc | Image

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Terms	Documents
(expandible)adj1(clay)same(smectite)	2

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Search Results - Record(s) 1 through 10 of 54 returned.

☐ 1. Document ID: US 20030183809 A1

L4: Entry 1 of 54 File: PGPB Oct 2, 2003

PGPUB-DOCUMENT-NUMBER: 20030183809
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030183809 A1

TITLE: Heat resistant organoclay

PUBLICATION-DATE: October 2, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Onikata, Masanobu	Gunma		JP	
Ohya, Mituru	Annaka-si		JP	
Kondo, Mitsuji	Annaka-si		JP	

US-CL-CURRENT: 252/397; 106/487

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image

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☐ 2. Document ID: US 20030176537 A1

L4: Entry 2 of 54 File: PGPB Sep 18, 2003

PGPUB-DOCUMENT-NUMBER: 20030176537
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030176537 A1

TITLE: Composite materials with improved phyllosilicate dispersion

PUBLICATION-DATE: September 18, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Chaiko, David J.	Naperville	IL	US	

US-CL-CURRENT: 523/200; 524/445, 524/449, 524/451

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image

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☐ 3. Document ID: US 20030162877 A1

L4: Entry 3 of 54 File: PGPB Aug 28, 2003

PGPUB-DOCUMENT-NUMBER: 20030162877

PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030162877 A1

TITLE: Process for the preparation of organoclays

PUBLICATION-DATE: August 28, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Chaiko, David J.	Napervill	IL	US	

US-CL-CURRENT: 524/445; 524/487

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw. Desc | Image

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☐ 4. Document ID: US 20030152531 A1

L4: Entry 4 of 54 File: PGPB Aug 14, 2003

PGPUB-DOCUMENT-NUMBER: 20030152531
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030152531 A1

TITLE: Multifunctional particulate additive for personal care and cosmetic compositions, and the process of making the same

PUBLICATION-DATE: August 14, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
SenGupta, Ashoke K.	Barrington	IL	US	
Spindler, Ralph	Palatine	IL	US	
Darlington, Jerald W. JR.	Marengo	IL	US	

US-CL-CURRENT: 424/59; 424/60

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw. Desc | Image

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☐ 5. Document ID: US 20030108705 A1

L4: Entry 5 of 54 File: PGPB Jun 12, 2003

PGPUB-DOCUMENT-NUMBER: 20030108705
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20030108705 A1

TITLE: Injection-molded water soluble container

PUBLICATION-DATE: June 12, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Duffield, Paul John	Beverley		GB	
Hammond, Geoffrey Robert	Hull		GB	
Edwards, David Brian	Stevenage		GB	
McCarthy, William John	Shaftesbury		GB	
Beckett, Arnold Heyworth	London		GB	
Jackman, Anthony Douglas	Woking		GB	

US-CL-CURRENT: 428/36.6; 53/285, 53/473, 53/509

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 6. Document ID: US 20020182155 A1

L4: Entry 6 of 54   File: PGPB   Dec 5, 2002

PGPUB-DOCUMENT-NUMBER: 20020182155
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020182155 A1

TITLE: Multifunctional particulate additive for personal care and cosmetic compositions, and the process of making the same

PUBLICATION-DATE: December 5, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
SenGupta, Ashoke K.	Barrington	IL	US	
Spindler, Ralph	Palatine	IL	US	
Darlington, Jerald W. JR.	Marengo	IL	US	

US-CL-CURRENT: 424/59; 424/400, 424/401, 424/60, 424/78.02, 424/78.08

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 7. Document ID: US 20020143094 A1

L4: Entry 7 of 54   File: PGPB   Oct 3, 2002

PGPUB-DOCUMENT-NUMBER: 20020143094
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020143094 A1

TITLE: Polymer nanocomposites and methods of preparation

PUBLICATION-DATE: October 3, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Conroy, Jeffrey L.	Rumford	RI	US	
Piche, Joseph W.	Raynham	MA	US	
Glatkowski, Paul J.	Littleton	MA	US	
Landis, David H.	Barrington	RI	US	

US-CL-CURRENT: 524/445; 524/449

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 8. Document ID: US 20020085983 A1

L4: Entry 8 of 54   File: PGPB   Jul 4, 2002

PGPUB-DOCUMENT-NUMBER: 20020085983
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020085983 A1

TITLE: Segmented composition and a method and a system for making same

PUBLICATION-DATE: July 4, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Fleissman, Leona G.	Ridgewood	NJ	US	
Santini, Anthony M.	Yonkers	NY	US	

US-CL-CURRENT: 424/64

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 9. Document ID: US 20010008633 A1

L4: Entry 9 of 54   File: PGPB   Jul 19, 2001

PGPUB-DOCUMENT-NUMBER: 20010008633
PGPUB-FILING-TYPE: new-utility
DOCUMENT-IDENTIFIER: US 20010008633 A1

TITLE: Cosmetic stick

PUBLICATION-DATE: July 19, 2001

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Travkina, Irina	River Edge	NJ	US	
Raouf, Maha	Franklin Lakes	NJ	US	
Pahlck, Harold	Waldwick	NJ	US	

US-CL-CURRENT: 424/401; 510/130

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 10. Document ID: US 6627598 B1

L4: Entry 10 of 54   File: USPT   Sep 30, 2003

US-PAT-NO: 6627598
DOCUMENT-IDENTIFIER: US 6627598 B1

TITLE: Solid detergent compositions comprising an organophilic smectite clay

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments

KWIC | Draw Desc | Image

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Terms	Documents
L3 and (solvent)same(water)	54

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Search Results - Record(s) 11 through 20 of 54 returned.

☐ 11. Document ID: US 6593285 B1

L4: Entry 11 of 54 File: USPT Jul 15, 2003

US-PAT-NO: 6593285
DOCUMENT-IDENTIFIER: US 6593285 B1

TITLE: Alkylbenzenesulfonate surfactants

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 12. Document ID: US 6583096 B1

L4: Entry 12 of 54 File: USPT Jun 24, 2003

US-PAT-NO: 6583096
DOCUMENT-IDENTIFIER: US 6583096 B1

TITLE: Laundry detergents comprising modified alkylbenzene sulfonates

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 13. Document ID: US 6521690 B1

L4: Entry 13 of 54 File: USPT Feb 18, 2003

US-PAT-NO: 6521690
DOCUMENT-IDENTIFIER: US 6521690 B1

TITLE: Smectite clay/organic chemical/polymer compositions useful as nanocomposites

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 14. Document ID: US 6521678 B1

L4: Entry 14 of 54 File: USPT Feb 18, 2003

US-PAT-NO: 6521678
DOCUMENT-IDENTIFIER: US 6521678 B1

TITLE: Process for the preparation of organoclays

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 15. Document ID: US 6500411 B2

L4: Entry 15 of 54 File: USPT Dec 31, 2002

US-PAT-NO: 6500411
DOCUMENT-IDENTIFIER: US 6500411 B2

TITLE: Multifunctional particulate additive for personal care and cosmetic compositions, and the process of making the same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 16. Document ID: US 6465543 B1

L4: Entry 16 of 54 File: USPT Oct 15, 2002

US-PAT-NO: 6465543
DOCUMENT-IDENTIFIER: US 6465543 B1

TITLE: Polyolefin nanocomposites

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 17. Document ID: US 6391449 B1

L4: Entry 17 of 54 File: USPT May 21, 2002

US-PAT-NO: 6391449
DOCUMENT-IDENTIFIER: US 6391449 B1
**** See image for Certificate of Correction ****

TITLE: Polymer/clay intercalates, exfoliates, and nanocomposites comprising a clay mixture and a process for making same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 18. Document ID: US 6380295 B1

L4: Entry 18 of 54 File: USPT Apr 30, 2002

US-PAT-NO: 6380295
DOCUMENT-IDENTIFIER: US 6380295 B1

TITLE: Clay/organic chemical compositions useful as additives to polymer, plastic and resin matrices to produce nanocomposites and nanocomposites containing such compositions

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 19. Document ID: US 6365139 B2

L4: Entry 19 of 54 File: USPT Apr 2, 2002

US-PAT-NO: 6365139

DOCUMENT-IDENTIFIER: US 6365139 B2
** See image for Certificate of Correction **

TITLE: Cosmetic stick

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 20. Document ID: US 6288076 B1

L4: Entry 20 of 54   File: USPT   Sep 11, 2001

US-PAT-NO: 6288076
DOCUMENT-IDENTIFIER: US 6288076 B1

TITLE: Antimicrobial compositions

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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Terms	Documents
L3 and (solvent)same(water)	54

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Search Results - Record(s) 21 through 30 of 54 returned.

☐ 21. Document ID: US 6287634 B1
L4: Entry 21 of 54 File: USPT Sep 11, 2001

US-PAT-NO: 6287634
DOCUMENT-IDENTIFIER: US 6287634 B1

TITLE: Intercalates and exfoliates formed with monomeric ethers and esters; composite materials containing same methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw. Desc | Image

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☐ 22. Document ID: US 6183760 B1
L4: Entry 22 of 54 File: USPT Feb 6, 2001

US-PAT-NO: 6183760
DOCUMENT-IDENTIFIER: US 6183760 B1

TITLE: Cosmetic stick

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw. Desc | Image

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☐ 23. Document ID: US 6103687 A
L4: Entry 23 of 54 File: USPT Aug 15, 2000

US-PAT-NO: 6103687
DOCUMENT-IDENTIFIER: US 6103687 A
**** See image for Certificate of Correction ****

TITLE: Non-volatile quaternary ammonium compositions and their uses

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw. Desc | Image

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☐ 24. Document ID: US 6015816 A
L4: Entry 24 of 54 File: USPT Jan 18, 2000

US-PAT-NO: 6015816
DOCUMENT-IDENTIFIER: US 6015816 A

TITLE: Antimicrobial compositions

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw. Desc | Image

☐ 25. Document ID: US 5998528 A
L4: Entry 25 of 54 File: USPT Dec 7, 1999

US-PAT-NO: 5998528
DOCUMENT-IDENTIFIER: US 5998528 A

TITLE: Viscous carrier compositions, including gels, formed with an organic liquid carrier, a layered material: polymer complex, and a di-, and/or tri-valent cation

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 26. Document ID: US 5955094 A
L4: Entry 26 of 54 File: USPT Sep 21, 1999

US-PAT-NO: 5955094
DOCUMENT-IDENTIFIER: US 5955094 A

TITLE: Intercalates and exfoliates formed with organic pesticides compounds and compositions containing the same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 27. Document ID: US 5882662 A
L4: Entry 27 of 54 File: USPT Mar 16, 1999

US-PAT-NO: 5882662
DOCUMENT-IDENTIFIER: US 5882662 A

TITLE: Cosmetic compositions containing smectite gels

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 28. Document ID: US 5880197 A
L4: Entry 28 of 54 File: USPT Mar 9, 1999

US-PAT-NO: 5880197
DOCUMENT-IDENTIFIER: US 5880197 A

TITLE: Intercalates and exfoliates formed with monomeric amines and amides: composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 29. Document ID: US 5879589 A
L4: Entry 29 of 54 File: USPT Mar 9, 1999

US-PAT-NO: 5879589
DOCUMENT-IDENTIFIER: US 5879589 A

TITLE: Process for antistatic treatment of resin and antistatic resin composition

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 30. Document ID: US 5877248 A

L4: Entry 30 of 54   File: USPT   Mar 2, 1999

US-PAT-NO: 5877248
DOCUMENT-IDENTIFIER: US 5877248 A
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with oligomers and polymers and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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Terms	Documents
L3 and (solvent)same(water)	54

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Search Results - Record(s) 31 through 40 of 54 returned.

☐ 31. Document ID: US 5844032 A

L4: Entry 31 of 54 File: USPT Dec 1, 1998

US-PAT-NO: 5844032
DOCUMENT-IDENTIFIER: US 5844032 A

TITLE: Intercalates and exfoliates formed with non-EVOH monomers, oligomers and polymers; and EVOH composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 32. Document ID: US 5804613 A

L4: Entry 32 of 54 File: USPT Sep 8, 1998

US-PAT-NO: 5804613
DOCUMENT-IDENTIFIER: US 5804613 A
**** See image for Certificate of Correction ****

TITLE: Intercalates and exfoliates formed with monomeric carbonyl-functional organic compounds, including carboxylic and polycarboxylic acids; aldehydes; and ketones; composite materials containing same and methods of modifying rheology therewith

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 33. Document ID: US 5780618 A

L4: Entry 33 of 54 File: USPT Jul 14, 1998

US-PAT-NO: 5780618
DOCUMENT-IDENTIFIER: US 5780618 A

TITLE: Oxidized cellulose

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 34. Document ID: US 5760121 A

L4: Entry 34 of 54 File: USPT Jun 2, 1998

US-PAT-NO: 5760121
DOCUMENT-IDENTIFIER: US 5760121 A

TITLE: Intercalates and exfoliates formed with oligomers and polymers and composite materials containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 35. Document ID: US 5759938 A

L4: Entry 35 of 54 File: USPT Jun 2, 1998

US-PAT-NO: 5759938
DOCUMENT-IDENTIFIER: US 5759938 A

TITLE: Process for producing organoclays with quaternary ammonium compositions made using non volatile diluents

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 36. Document ID: US 5730996 A

L4: Entry 36 of 54 File: USPT Mar 24, 1998

US-PAT-NO: 5730996
DOCUMENT-IDENTIFIER: US 5730996 A

TITLE: Intercalates and expoliates formed with organic pesticide compounds and compositions containing the same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 37. Document ID: US 5721306 A

L4: Entry 37 of 54 File: USPT Feb 24, 1998

US-PAT-NO: 5721306
DOCUMENT-IDENTIFIER: US 5721306 A

TITLE: Viscous carrier compositions, including gels, formed with an organic liquid carrier and a layered material:polymer complex

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 38. Document ID: US 5634969 A

L4: Entry 38 of 54 File: USPT Jun 3, 1997

US-PAT-NO: 5634969
DOCUMENT-IDENTIFIER: US 5634969 A

TITLE: Organoclay compositions

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

☐ 39. Document ID: US 5573583 A

L4: Entry 39 of 54 File: USPT Nov 12, 1996

US-PAT-NO: 5573583
DOCUMENT-IDENTIFIER: US 5573583 A
**** See image for Certificate of Correction ****

TITLE: Method of activation of clay and activated clay

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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☐ 40. Document ID: US 5468701 A
L4: Entry 40 of 54 File: USPT Nov 21, 1995

US-PAT-NO: 5468701
DOCUMENT-IDENTIFIER: US 5468701 A
**** See image for Certificate of Correction ****

TITLE: Process for regenerating spent acid-activated bentonite clays and smectite catalysts

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments   KWIC | Draw Desc | Image

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Terms	Documents
L3 and (solvent)same(water)	54

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Search Results - Record(s) 41 through 50 of 54 returned.

☐ 41. Document ID: US 5414079 A

L4: Entry 41 of 54 File: USPT May 9, 1995

US-PAT-NO: 5414079
DOCUMENT-IDENTIFIER: US 5414079 A

TITLE: Oxidized cellulose

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 42. Document ID: US 5358915 A

L4: Entry 42 of 54 File: USPT Oct 25, 1994

US-PAT-NO: 5358915
DOCUMENT-IDENTIFIER: US 5358915 A
**** See image for Certificate of Correction ****

TITLE: Process for regenerating spent acid-activated bentonite clays and smectite catalysts

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 43. Document ID: US 5214218 A

L4: Entry 43 of 54 File: USPT May 25, 1993

US-PAT-NO: 5214218
DOCUMENT-IDENTIFIER: US 5214218 A

TITLE: One step synthesis of methyl t-butyl ether from t-butanol using haloacid-modified clay catalysts

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 44. Document ID: US 5191130 A

L4: Entry 44 of 54 File: USPT Mar 2, 1993

US-PAT-NO: 5191130
DOCUMENT-IDENTIFIER: US 5191130 A

TITLE: Process for oligomerizing olefins using halogenated phosphorous-containing acid on montmorillonite clay

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 45. Document ID: US 5183947 A

L4: Entry 45 of 54 File: USPT Feb 2, 1993

US-PAT-NO: 5183947
DOCUMENT-IDENTIFIER: US 5183947 A

TITLE: One step synthesis of methyl t-butyl ether from t-butanol using fluorophosphoric acid-modified clay catalysts

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 46. Document ID: US 5157161 A

L4: Entry 46 of 54 File: USPT Oct 20, 1992

US-PAT-NO: 5157161
DOCUMENT-IDENTIFIER: US 5157161 A

TITLE: One-step synthesis of methyl t-butyl ether from t-butanol using hydrogen fluoride-modified montmorillonite clays

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 47. Document ID: US 4960740 A

L4: Entry 47 of 54 File: USPT Oct 2, 1990

US-PAT-NO: 4960740
DOCUMENT-IDENTIFIER: US 4960740 A

TITLE: Organophilic clay compositions

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 48. Document ID: US 4913828 A

L4: Entry 48 of 54 File: USPT Apr 3, 1990

US-PAT-NO: 4913828
DOCUMENT-IDENTIFIER: US 4913828 A

TITLE: Conditioning agents and compositions containing same

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 49. Document ID: US 4740488 A

L4: Entry 49 of 54 File: USPT Apr 26, 1988

US-PAT-NO: 4740488
DOCUMENT-IDENTIFIER: US 4740488 A

TITLE: Modified clay sorbents

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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☐ 50. Document ID: US 4626364 A

L4: Entry 50 of 54 File: USPT Dec 2, 1986

US-PAT-NO: 4626364
DOCUMENT-IDENTIFIER: US 4626364 A

TITLE: Particulate fabric softening and antistatic built detergent composition and particulate agglomerate for use in manufacture thereof

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC | Draw Desc | Image

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Terms	Documents
L3 and (solvent)same(water)	54

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Search Results - Record(s) 51 through 54 of 54 returned.

☐ 51. Document ID: US 4536315 A

L4: Entry 51 of 54 File: USPT Aug 20, 1985

US-PAT-NO: 4536315
DOCUMENT-IDENTIFIER: US 4536315 A

TITLE: Perfume-containing carrier having surface-modified particles for laundry composition

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 52. Document ID: US 4495292 A

L4: Entry 52 of 54 File: USPT Jan 22, 1985

US-PAT-NO: 4495292
DOCUMENT-IDENTIFIER: US 4495292 A

TITLE: Determination of expandable clay minerals at well sites

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 53. Document ID: JP 06157947 A

L4: Entry 53 of 54 File: JPAB Jun 7, 1994

PUB-NO: JP406157947A
DOCUMENT-IDENTIFIER: JP 06157947 A
TITLE: TRANSPARENT COATING

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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☐ 54. Document ID: JP 04240857 A

L4: Entry 54 of 54 File: JPAB Aug 28, 1992

PUB-NO: JP404240857A
DOCUMENT-IDENTIFIER: JP 04240857 A
TITLE: ELECTROSTATIC RECORDING BODY

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments KWIC | Draw Desc | Image

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Terms	Documents
L3 and (solvent)same(water)	54

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L7: Entry 31 of 38 File: USPT Feb 24, 1998

US-PAT-NO: 5721306
DOCUMENT-IDENTIFIER: US 5721306 A

TITLE: Viscous carrier compositions, including gels, formed with an organic liquid carrier and a layered material:polymer complex

DATE-ISSUED: February 24, 1998

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Tsipursky; Semeon	Lincolnwood	IL		
Beall; Gary W.	McHenry	IL		
Sorokin; Anatoliy	Buffalo Grove	IL		
Goldman; Anatoliy	Palatine	IL		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
AMCOL International Corporation	Arlington Heights	IL			02

APPL-NO: 08/ 525416 [PALM]
DATE FILED: September 8, 1995

PARENT-CASE:
CROSS-REFERENCE TO RELATED APPLICATIONS This application is a continuation-in-part of application Ser. Nos. 08/488,264; now U.S. Pat. Nos. 5,552,469 Ser. No. 08/480,080 now U.S. Pat. No. 5,578,672 and Ser. No. 08/488,263, pending all filed Jun. 7, 1998.

INT-CL: [06] C08 K 3/34, C08 K 5/10, C08 K 5/06, C08 K 5/05

US-CL-ISSUED: 524/449; 523/203, 523/207, 523/209, 523/212, 523/216, 524/312, 524/376, 524/377, 524/445, 524/446, 524/447, 524/451, 524/548, 524/557, 524/702, 524/789, 524/791, 524/379, 524/386, 501/4
US-CL-CURRENT: 524/449; 501/4, 523/203, 523/207, 523/209, 523/212, 523/216, 524/312, 524/376, 524/377, 524/379, 524/386 , 524/445, 524/446, 524/447, 524/451, 524/548, 524/557, 524/702, 524/789, 524/791

FIELD-OF-SEARCH: 524/449, 524/445, 524/446, 524/447, 524/789, 524/791, 524/376, 524/377, 524/312, 524/702, 524/451, 524/548, 524/557, 524/379, 524/386, 523/203, 523/212, 523/207, 523/209, 523/216, 501/4

PRIOR-ART-DISCLOSED:

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Search Selected | Search ALL

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
3419460	December 1968	Ure	161/162

☐	3419517	December 1968	Hedrick et al.	260/37
☐	3515626	June 1970	Duffield	161/162
☐	3773708	November 1973	Takahashi et al.	260/41R
☐	3795650	March 1974	Burns	260/33.4R
☐	3912532	October 1975	Simone	106/308N
☐	3929678	December 1975	Laughlin et al.	252/526
☐	4125411	November 1978	Lyons	106/291
☐	4210572	July 1980	Herman et al.	260/404
☐	4251576	February 1981	Osborn et al.	428/331
☐	4400485	August 1983	Mukamal et al.	524/444
☐	4431755	February 1984	Weber et al.	523/203
☐	4434075	February 1984	Mardis et al.	252/315.2
☐	4472538	September 1984	Kamigaito et al.	523/202
☐	4500670	February 1985	McKinley et al.	524/445
☐	4546145	October 1985	Kishida et al.	524/780
☐	4600744	July 1986	Libor et al.	524/446
☐	4613542	September 1986	Alexander	428/290
☐	4624982	November 1986	Alexander	524/446
☐	4739007	April 1988	Okada et al.	524/789
☐	4789403	December 1988	Rice	106/417
☐	4798766	January 1989	Rice	428/404
☐	4810734	March 1989	Kawasumi et al.	523/216
☐	4842651	June 1989	Ravet et al.	106/487
☐	4889885	December 1989	Usuki et al.	524/443
☐	4894411	January 1990	Okada et al.	524/710
☐	4920171	April 1990	Hutton, Jr. et al.	524/446
☐	5032546	July 1991	Giannelis et al.	501/3
☐	5032547	July 1991	Giannelis et al.	501/3
☐	5091462	February 1992	Fukui et al.	524/504
☐	5102948	April 1992	Deguchi et al.	524/789
☐	5164440	November 1992	Deguchi et al.	524/444
☐	5164460	November 1992	Yano et al.	624/445
☐	5204078	April 1993	Tateyama et al.	423/331
☐	5206284	April 1993	Fukui et al.	524/504
☐	5229451	July 1993	Carter et al.	524/493
☐	5248720	September 1993	Deguchi et al.	524/444
☐	5326500	July 1994	Friedman et al.	252/378
☐	5340558	August 1994	Friedman et al.	423/328.1
☐	5385776	January 1995	Maxfield et al.	428/297
☐	5391437	February 1995	Miyasaka et al.	524/446
☐	5414042	May 1995	Yasue et al.	524/789
☐	5428094	June 1995	Tokoh et al.	524/446
☐	5506046	April 1996	Andersen et al.	524/446

☐	5508072	April 1996	Andersen et al.	524/446

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0 205 281 A3	December 1986	EP	
0 335 653 A1	October 1989	EP	
0 358 415 A1	March 1990	EP	
0 479 031 A1	April 1992	EP	
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WO 93/04117	March 1993	WO	

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Search Report for WO 93/04118 which was submitted with Applicants' Information Disclosure Statement filed Dec. 5, 1995, identified as B3.

ART-UNIT: 151

PRIMARY-EXAMINER: Szekely; Peter A.

ATTY-AGENT-FIRM: Marshall, O'Toole, Gerstein, Murray & Borun

ABSTRACT:

Intercalates formed by contacting the layer material, e.g., a phyllosilicate, with an intercalant polymer to sorb or intercalate the polymer between adjacent platelets of the layered material. Sufficient intercalant polymer is sorbed between adjacent platelets to expand the adjacent platelets to a spacing of at least about 50 .ANG. (as measured after water removal to a maximum of 5% by weight water), up to about 100 .ANG. and preferably in the range of about 10-45 .ANG., so that the intercalate easily can be exfoliated into individual platelets. The intercalated complex is combined with an organic liquid into an unexpectedly viscous carrier material, for delivery of the carrier material, or for delivery of an active compound, e.g., a pharmaceutical, or cosmetic, or lubricant, e.g., food guide lubricants dissolved or dispersed in the carrier material. Alternatively, the intercalated complex can be exfoliated prior to combination with the organic liquid.

90 Claims, 17 Drawing figures
Exemplary Claim Number: 1
Number of Drawing Sheets: 16

BRIEF SUMMARY:

1 FIELD OF THE INVENTION

2 The present invention is directed to viscous carrier or viscous solvent compositions useful for carrying active organic compounds, such as glycols; glycerols; alcohols; ketones; and other organic liquids; ~~pigments~~; drugs; skin moisturizers; hair care compounds, e.g., silicone oils and silicone fluids; permanent waving lotion and hair relaxer reducing agents, and other hair care compounds, such as moisturizers, shampoos, hair conditioners, and shampoos/conditioners; oven cleaners; car wash compositions; cosmetics; alcohols and other de-icers for airplane wings and the like; lotions, ointments and creams; drug carriers for various pharmaceuticals and drugs, particularly for topical administration of medications, such as topical wound and burn medicaments. The viscous carrier compositions are formed from intercalated layered materials, and/or exfoliates thereof, manufactured by sorption of one or more intercalant compounds, e.g., oligomers or polymers between planar layers of a swellable layered material, such as a phyllosilicate or other layered material, to expand the interlayer spacing of adjacent layers to at least about 5 .ANG., preferably at least about 10 .ANG.. The intercalates and/or exfoliates are combined with an organic liquid carrier to viscosify the carrier. The intercalates and exfoliates are described in our above-identified co-pending parent applications. The intercalated layered materials preferably have at least two layers of oligomer and/or polymer molecules sorbed on the internal surfaces between adjacent layers of the planar platelets of the layered material, such as a phyllosilicate,

preferably a smectite clay, to expand the interlayer spacing to at least about 5 Angstroms, preferably at least about 10 Angstroms, more preferably to at least about 20 Angstroms, and most preferably to at least about 30-45 Angstroms, up to about 100 .ANG., or disappearance of periodicity. The resulting intercalates are neither entirely organophilic nor entirely hydrophilic, but a combination of the two, and easily can be exfoliated for or during admixture with a carrier or solvent to provide a stable, thixotropic composition, preferably a stable gel, capable of carrying any liquid hydrophilic or hydrophobic compound, particularly organic liquid compounds, and combinations of hydrophilic and hydrophobic liquids.

3 BACKGROUND OF THE INVENTION AND PRIOR ART

4 It is well known that phyllosilicates, such as smectite clays, e.g., sodium montmorillonite and calcium montmorillonite, can be treated with organic molecules, such as organic ammonium ions, to intercalate the organic molecules between adjacent, planar silicate layers, thereby substantially increasing the interlayer (interlaminar) spacing between the adjacent silicate layers. The thus-treated, intercalated phyllosilicates, then can be exfoliated, e.g., the silicate layers are separated, e.g., mechanically, by high shear mixing. The individual silicate layers, when admixed with a matrix polymer, before, after or during the polymerization of the matrix polymer, e.g., a polyamide--see U.S. Pat. Nos. 4,739,007; 4,810,734; and 5,385,776--have been found to substantially improve one or more properties of the polymer, such as mechanical strength and/or high temperature characteristics.

5 Exemplary of such prior art composites, also called "nanocomposites", are disclosed in published PCT disclosure of Allied Signal, Inc. WO 93/04118 and U.S. Pat. No. 5,385,776, disclosing the admixture of individual platelet particles derived from intercalated layered silicate materials, with a polymer to form a polymer matrix having one or more properties of the matrix polymer improved by the addition of the exfoliated intercalate. As disclosed in WO 93/04118, the intercalate is formed (the interlayer spacing between adjacent silicate platelets is increased) by adsorption of a silane coupling agent or an onium cation, such as a quaternary ammonium compound, having a reactive group which is compatible with the matrix polymer. Such quaternary ammonium cations are well known to convert a highly hydrophilic clay, such as sodium or calcium montmorillonite, into an organophilic clay capable of sorbing organic molecules. A publication that discloses direct intercalation (without solvent) of polystyrene and poly(ethylene oxide) in organically modified silicates is Synthesis and Properties of Two-Dimensional Nanostructures by Direct Intercalation of Polymer Melts in Layered Silicates, Richard A. Vaia, et al., Chem. Mater., 5:1694-1696(1993). Also as disclosed in Adv. Materials, 7, No. 2: (1985), pp, 154-156, New Polymer Electrolyte Nanocomposites: Melt Intercalation of Poly(Ethylene Oxide) in Mica-Type Silicates, Richard A. Vaia, et al., poly(ethylene oxide) can be intercalated directly into Na-montmorillonite and Li-montmorillonite by heating to 80.degree. C. for 2-6 hours to achieve a d-spacing of 17.7 .ANG.. The intercalation is accompanied by displacing water molecules, disposed between the clay platelets with polymer molecules. Apparently, however, the intercalated material could not be exfoliated and was tested in pellet form. It was quite surprising to one of the authors of these articles that exfoliated material could be manufactured in accordance with the present invention.

6 Previous attempts have been made to intercalate polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVOH) and poly(ethylene oxide) (PEO) between montmorillonite clay platelets with little success. As described in Levy, et al., Interlayer Adsorption of Polyvinylpyrrolidone on Montmorillonite, Journal of Colloid and Interface Science, Vol. 50, No. 3, March 1975, pages 442-450, attempts were made to sorb PVP (40,000 average M.W.) between monoionic montmorillonite clay platelets (Na, K, Ca and Mg) by successive washes with absolute ethanol, and then attempting to sorb the PVP by contact with 1% PVP/ethanol/water solutions, with varying amounts of water, via replacing the ethanol solvent molecules that were sorbed in washing (to expand the platelets to about 17.7 .ANG.). Only the sodium montmorillonite had expanded beyond a 20 .ANG. basal spacing (e.g., 26 .ANG. and 32 .ANG.), at 5.sup.+ % H.sub.2 O, after contact with the PVP/ethanol/H.sub.2 O solution. It was concluded that the ethanol was needed to initially increase the

basal spacing for later sorption of PVP, and that water did not directly affect the sorption of PVP between the clay platelets (Table II, page 445), except for sodium montmorillonite. The sorption was time consuming and difficult and met with little success.

7 Further, as described in Greenland, Adsorption of Polyvinyl Alcohols by Montmorillonite, Journal of Colloid Sciences, Vol. 18, pages 647-664 (1963), polyvinyl alcohols containing 12% residual acetyl groups could increase the basal spacing by only about 10 .ANG. due to the sorbed polyvinyl alcohol (PVOH). As the concentration of polymer in the intercalant polymer-containing solution was increased from 0.25% to 4%, the amount of polymer sorbed was substantially reduced, indicating that sorption might only be effective at polymer concentrations in the intercalant polymer-containing composition on the order of 1% by weight polymer, or less. Such a dilute process for intercalation of polymer into layered materials would be exceptionally costly in drying the intercalated layered materials for separation of intercalate from the polymer carrier, e.g., water, and, therefore, apparently no further work was accomplished toward commercialization.

8 In accordance with one embodiment of the present invention, intercalates are prepared by contacting a phyllosilicate with a PVP polymer, preferably essentially alcohol-free, or a PVOH intercalant polymer composition, wherein the PVOH preferably contains 5% or less residual acetyl groups, more preferably fully hydrolyzed, containing 1% or less acetyl groups.

9 In accordance with an important feature of the present invention, best results are achieved using a water soluble oligomer (herein defined as a prepolymer having 2 to about 15 recurring monomeric units, which can be the same or different) or polymer (herein defined as having more than about 15 recurring monomeric units, which can be the same or different) composition for intercalation having at least about 2%, preferably at least about 5% by weight, more preferably at least about 10% by weight intercalant oligomer or intercalant polymer concentration, most preferably about 30% to about 80% by weight oligomer and/or polymer, based on the weight of oligomer and/or polymer and carrier (e.g., water with or without another solvent for the intercalant oligomer or intercalant polymer) to achieve better sorption of the intercalant polymers between phyllosilicate platelets. Regardless of the concentration of polymer in liquid solvent of the intercalating composition, the intercalating composition should have a polymer:layered material ratio of at least 1:20, preferably at least 1:10, more preferably at least 1:5, and most preferably about 1:4 to achieve efficient intercalation of the polymer between adjacent platelets of the layered material. The oligomer or polymer sorbed between and permanently bonded to the silicate platelets causes separation or added spacing between adjacent silicate platelets and, for simplicity of description, both the oligomers and polymers are hereinafter called the "intercalant" or "intercalant polymer" or "polymer intercalant". In this manner, the oligomers or polymers will be sorbed sufficiently to increase the interlayer spacing of the phyllosilicate in the range of about 5 .ANG. to about 100 .ANG., preferably at least about 10 .ANG., for easier and more complete exfoliation, in a commercially viable process, regardless of the particular phyllosilicate or intercalant polymer.

10 A phyllosilicate, such as a smectite clay, can be intercalated sufficiently for subsequent exfoliation by sorption of polymers or oligomers that have carbonyl, hydroxyl, carboxyl, amine, amide, ether, ester, sulfate, sulfonate, sulfinate, sulfamate, phosphate, phosphonate, phosphinate functionalities, or aromatic rings to provide metal cation chelate-type bonding between two functional groups of one or two intercalant polymer molecules and the metal cations bonded to the inner surfaces of the phyllosilicate platelets. Sorption and metal cation electrostatic attraction or bonding of a platelet metal cation between two oxygen or nitrogen atoms of the molecules; or the electrostatic bonding between the interlayer cations in hexagonal or pseudohexagonal rings of the smectite layers and an intercalant polymer aromatic ring structure increases the interlayer spacing between adjacent silicate platelets or other layered material to at least about about 5 .ANG., preferably at least about 10 .ANG., and more preferably at least about 20 .ANG., and most preferably in the range of about 30 .ANG. to about 45

.ANG.. Such intercalated phyllosilicates easily can be exfoliated into individual phyllosilicate platelets before or during admixture with a liquid carrier or solvent, for example, one or more monohydric alcohols, such as methanol, ethanol, propanol, and/or butanol; polyhydric alcohols, such as glycerols and glycols, e.g., ethylene glycol, propylene glycol, butylene glycol, glycerine and mixtures thereof; aldehydes, ketones, carboxylic acids; amines; amides; and other solvents, for delivery of the solvent in a thixotropic composition, or for delivery of any active hydrophobic or hydrophilic organic compound, such as a typically active pharmaceutical, dissolved or dispersed in the carrier or solvent, in a thixotropic composition.

11 Depending upon the conditions that the composition is subjected to during intercalation and exfoliation, particularly temperature; pH; and amount of water contained in the intercalating composition, the intercalate and/or exfoliate/carrier composition can be formed to any desired viscosity, e.g., at least about 100 centipoises, preferably at least about 500-1000 centipoises, whether or not gelled, and particularly to extremely high viscosities of about 5,000 to about 5,000,000 centipoises. The compositions are thixotropic so that shearing will lower viscosity for easier delivery, and then by reducing shear or eliminating shear, the compositions will increase in viscosity. The intercalant polymer intercalates between the spaces of adjacent platelets of the layered material for easy exfoliation, and complexes with the metal cations on the platelet surfaces where the polymer remains after the intercalant, or exfoliate thereof, is combined with the carrier/solvent. It is theorized that the polymer coating on the surfaces of the clay platelets is ionically complexed with interlayer cations and participates (aids) in the viscosification and thixotropy of the carrier/solvent composition. However, other forms of bonding such as hydrogen bonding or Van Der Waals forces or molecular complexing also may be responsible for the adherence of the polymer to the surfaces of the layered material, either entirely, or in part.

12 DEFINITIONS

13 Whenever used in this Specification, the terms set forth shall have the following meanings:

14 "Layered Material" shall mean an inorganic material, such as a smectite clay mineral, that is in the form of a plurality of adjacent, bound layers and has a thickness, for each layer, of about 3 .ANG. to about 50 .ANG., preferably about 10 .ANG..

15 "Platelets" shall mean individual layers of the Layered Material.

16 "Intercalate" or "Intercalated" shall mean a Layered Material that includes oligomer and/or polymer molecules disposed between adjacent platelets of the Layered Material to increase the interlayer spacing between the adjacent platelets to at least about 5 .ANG., preferably at least about 10 .ANG..

17 "Intercalation" shall mean a process for forming an Intercalate.

18 "Intercalant Polymer" or "Intercalant" shall mean an oligomer or polymer that is sorbed between Platelets of the Layered Material and complexes with the platelet surfaces to form an Intercalate.

19 "Intercalating Carrier" shall mean a carrier comprising water with or without an organic solvent used together with an Intercalant Polymer to form an Intercalating Composition capable of achieving Intercalation of the Layered Material.

20 "Intercalating Composition" shall mean a composition comprising an Intercalant Polymer, an Intercalating Carrier for the Intercalant Polymer, and a Layered Material.

21 "Exfoliate" or "Exfoliated" shall mean individual platelets of an Intercalated Layered Material so that adjacent platelets of the Intercalated Layered Material can be dispersed individually throughout a carrier material, such as water, an

alcohol or glycol, or any other organic solvent.

22 "Exfoliation" shall mean a process for forming an Exfoliate from an Intercalate.

23 SUMMARY OF THE INVENTION

24 In brief, the present invention is directed to viscous, thixotropic carrier compositions comprising a liquid carrier or solvent composition containing intercalated and/or exfoliated platelets of a layered material. The intercalated layered material is formed by contacting a layered material, such as a phyllosilicate, with an oligomer and/or polymer to sorb or intercalate the intercalant polymer or mixtures of intercalant polymers between adjacent phyllosilicate platelets. Sufficient intercalant polymer is sorbed between adjacent phyllosilicate platelets to expand the spacing between adjacent platelets (interlayer spacing) to a distance of at least about 5 .ANG., preferably at least about 10 .ANG. (as measured after water removal to a maximum water content of 5% by weight) and preferably in the range of about 30-45 .ANG., so that the intercalate easily can be exfoliated, sometimes naturally, without shearing being necessary. At times, the intercalate requires shearing for exfoliation that easily can be accomplished, e.g., when mixing the intercalate with the carrier or solvent, to provide a composition of carrier or solvent and exfoliated platelets of the layered material having a desired viscosity of about 20 centipoises to about 5,000,000 centiposes, preferably at least about 500 centipoises.

25 The viscous compositions can be in the form of a stable thixotropic gel that is not subject to phase separation and can be used to deliver any active materials, such as in the cosmetic, hair care and pharmaceutical industries. The layered material is intercalated and optionally exfoliated by contact with an intercalant polymer and water and then mixed and/or extruded to intercalate the polymer between adjacent phyllosilicate platelets and optionally separate (exfoliate) the layered material into individual platelets. The amount of water varies, depending upon the amount of shear imparted to the layered material in contact with the polymer and water. In one method, the intercalating composition is pug milled or extruded. At a water content of about 25% by weight to about 50% by weight water, preferably about 35% to about 40% by weight water, based on the dry weight of the layered material, e.g., clay. In another method, the clay and water are slurried, with at least about 25% by weight water, based on the dry weight of the layered material, e.g., preferably less than about 20% by weight clay in water, based on the total weight of layered material and water, more preferably less than about 10% layered material in water, with the addition of about 2% by weight to about 90% by weight polymer, based on the dry weight of the layered material.

26 In accordance with a preferred embodiment of the present invention, the intercalant polymer should be water-soluble (herein defined as sufficiently soluble such that at least 0.1 gram of the polymer will dissolve per 100 grams of distilled water at 25.degree. C.). In accordance with a preferred embodiment of the present invention, the intercalant polymer should include an aromatic ring and/or have a functionality selected from the group consisting of a carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester, sulfate, solfonate, sulfinate, sulfamate, phosphate, phosphonate, phosphinate functionality, or an aromatic ring to be sufficiently complexed or bound to the platelet surfaces of the layered material. It is hereby theorized that polymer binding to the platelet surfaces is by metal cation electrostatic bonding or complexing, e.g., chelation, of the metal cations of the phyllosilicate sharing electrons with two carbonyl, two carboxyl, two hydroxyl, two oxygen, two amine, two SO.sub.x, two PO.sub.x (wherein x=2, 3, or 4) and/or two amide functionalities of one intercalant polymer molecule, or of two adjacent intercalant polymer molecules to an inner surface of the phyllosilicate platelets. Such intercalant polymers have sufficient affinity for the phyllosilicate platelets to provide sufficient interlayer spacing for exfoliation, e.g., about 5 .ANG.-100 .ANG., preferably about 10 .ANG.-50 .ANG., and to maintain attachment to the surfaces of the platelets, without the need for coupling agents or spacing agents, such as the onium ion or silane coupling agents disclosed in the above-mentioned prior art.

27 Sorption of the intercalant polymer should be sufficient to achieve expansion of

adjacent platelets of the layered material (when measured dry--having a maximum of about 5% by weight water) to an interlayer spacing of at least about 5 .ANG., preferably a spacing of at least about 10 .ANG., more preferably a spacing of at least about 20 .ANG., and most preferably a spacing of about 30-45 .ANG.. To achieve intercalates that can be exfoliated easily using the preferred water-soluble polymer intercalants disclosed herein, such as polyvinylpyrrolidone, polyvinyl alcohol, and mixtures thereof, the weight ratio of intercalant polymer to layered material, preferably a water-swellable smectite clay such as sodium bentonite, in the intercalating composition contacting the phyllosilicate should be at least about 1:20, preferably at least about 1:12 to 1:10, more preferably at least about 1:5, and most preferably about 1:5 to about 1:3. It is preferred that the concentration of polymer in the intercalating composition, based on the total weight of polymer plus intercalant carrier (water plus any organic liquid solvent) in the intercalating composition is at least about 15% by weight, more preferably at least about 20% by weight polymer, for example about 20%-30% to about 90% by weight polymer, based on the weight of polymer plus intercalant carrier (water plus any organic solvent) in the intercalant composition during intercalation.

28 It has been found that the intercalates of the present invention are increased in interlayer spacing step-wise. If the phyllosilicate is contacted with an intercalating composition containing less than about 16% by weight intercalant polymer, e.g., 10% to about 15% by weight polymer, based on the dry weight of the phyllosilicate, a monolayer width of intercalant polymer is sorbed (intercalated) between the adjacent platelets of the layered material. A monolayer of polymer intercalated between platelets increases the interlayer spacing to about 5 .ANG. to less than about 10 .ANG.. When the amount of intercalant polymer is in the range of about 16% to less than about 35% by weight, based on the weight of the dry layered material, the intercalant polymer is sorbed in a bilayer, and each layer complexes separately with one of two adjacent platelet surfaces, thereby increasing the interlayer spacing to about 10 .ANG. to about 16 .ANG., as shown in FIGS. 1 and 2. At an intercalant polymer loading in the intercalating composition of about 35% to less than about 55% intercalant polymer, based on the dry weight of the layered material in the intercalating composition, the interlayer spacing is increased to about 20 .ANG. to about 25 .ANG., corresponding to three layers of intercalant polymer sorbed between adjacent platelets of the layered material, as shown in FIGS. 1 and 2. At an intercalant polymer loading of about 55% to about 80% intercalant polymer, based on the dry weight of the layered material in the intercalating composition, the interlayer spacing will be increased to about 30 .ANG. to about 35 .ANG., corresponding to 4 and 5 layers of intercalant polymer sorbed (intercalated) between and complexed to adjacent platelets of the layered material, as shown in FIGS. 1 and 2.

29 Such interlayer spacings have never been achieved by direct intercalation of an oligomer or polymer molecule, without prior sorption of a coupling agent, such as an onium or silane coupling agent, and provides easier and more complete exfoliation for or during incorporation of the platelets into a carrier or solvent to provide unexpectedly viscous carrier compositions, for delivery of the carrier, or for administration of an active compound that is dissolved or dispersed in the carrier or solvent. Such compositions, especially the high viscosity gels, are particularly useful for delivery of active compounds, such as oxidizing agents for hair waving lotions, and drugs for topical administration, since extremely high viscosities are obtainable; and for admixtures of the platelets with polar solvents in modifying rheology, e.g., of cosmetics, oil-well drilling fluids, paints, lubricants, especially food grade lubricants in the manufacture of oil and grease, and the like.

30 Once exfoliated, the platelets of the intercalate are predominantly completely separated into individual platelets having intercalant polymer molecules complexed with the platelet surfaces, and the originally adjacent platelets no longer are retained in a parallel, spaced disposition, but are free to move as predominantly individual, polymer coated (continuously or discontinuously) platelets throughout a carrier or solvent material to maintain viscosity and thixotropy of the carrier material. The predominantly individual phyllosilicate platelets, having their platelet surfaces complexed with polymer molecules, are randomly, homogeneously and uniformly dispersed, predominantly as individual platelets, throughout the

carrier or solvent to achieve new and unexpected viscosities in the carrier/platelet compositions even after addition of an active organic compound, such as a cosmetic component or a medicament, for administration of the active organic compound(s) from the composition.

31 As recognized, the thickness of exfoliated, individual clay platelets (about 10 .ANG.) is relatively small compared to the size of the flat opposite polymer-complexed platelet faces. The clay platelets have an aspect ratio in the range of about 200 to about 2,000. Dispersing such finely divided platelet particles into an organic liquid carrier or solvent provides a very large area of contact between carrier and platelet particles, for a given volume of particles in the composition, and provides a high degree of platelet homogeneity and unexpectedly high viscosity to the composition.

32 The polymer intercalants used to form the intercalates and/or exfoliates used in the compositions of the present invention need not have any (but can include) reactivity with the carrier or solvent in which the inventive intercalates and/or exfoliates are dispersed, while improving one or more properties, particularly viscosity, of the carrier or solvent material.

DRAWING DESCRIPTION:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph plotting interlayer space for polyvinylpyrrolidone (PVP):smectite clay complexes (intercalates) showing d(001) and d(002) spacing, in Angstroms, between smectite clay platelets versus percentage of PVP sorbed, based on the dry weight of the smectite clay;

FIG. 2 is a graph plotting interlayer space for polyvinylalcohol (PVOH):smectite clay complexes (intercalates) showing d(001) spacing, in Angstroms, between smectite clay platelets versus percentage of PVOH sorbed, based on the dry weight of the smectite clay;

FIG. 3 is an x-ray diffraction pattern for a complex of PVP (weight average molecular weight of 10,000):sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 20:80;

FIG. 4 is an x-ray diffraction pattern for a complex of PVP (weight average molecular weight of 40,000):sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 20:80;

FIG. 5 is an x-ray diffraction pattern for a complex of PVOH (weight average molecular weight of 15,000):sodium montmorillonite clay, in Angstroms, at a weight ratio of PVOH:clay of 20:80;

FIG. 6 is an x-ray diffraction pattern for a complex of PVP:sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 20:80 (upper pattern); and an x-ray diffraction pattern for .apprxeq.100% sodium montmorillonite clay having a crystobalite impurity (lower pattern);

FIG. 7 is an x-ray diffraction pattern for a complex of PVP:sodium montmorillonite clay, in Angstroms, at a weight ratio of PVP:clay of 50:50 (upper pattern); and an x-ray diffraction pattern for .apprxeq.100% sodium montmorillonite clay having a crystobalite impurity (lower pattern); and

FIG. 8 is a portion of an x-ray diffraction pattern for PVP:sodium montmorillonite clay, in Angstroms, at a PVP:clay ratio of 80:20, showing a PVP:clay complex peak or d(001) spacing of about 41 .ANG..

FIG. 9 is a graph of composition viscosity at 24.degree. C. vs. spindle velosity r.p.m. for compositions of 10% by weight Na bentonite clay: polyvinylpyrrolidone (PVP) complex, 6% by weight water, and 84% by weight glycerol showing thixotropy at

increased and decreased shear, and increased viscosity with increased temperatures of intercalation in formation of the clay:PVP complex;

FIG. 10 is a graph similar to the graph of FIG. 9, at a different scale, showing the data from FIG. 9 along the horizontal axis, and showing an unexpected increase in viscosity achieved by heating the composition gel to a temperature of 145.degree. C. before cooling and increasing viscosity at 24.degree. C.;

FIG. 11 is a graph of composition viscosity at 24.degree. C. of compositions containing 5% clay:PVP complex and 10% by weight Na bentonite:PVp complex (4:1 weight ratio for both) mixed with water and glycerol with various amounts of water (water plus glycerol equals 100%) showing an increase in viscosity from about 500,000 centipoises to about 3,000,000 centipoises by increasing the water content from 0% (100% glycerol) to about 7.5% water, and a decrease in viscosity with the addition of more than 7.5% water;

FIGS. 12 and 13 are graphs, at different scales, of composition viscosity at 24.degree. C. of compositions containing 5% by weight Na bentonite clay: PVP complex (4:1 weight ratio); 0-6% by weight water; and 89-95% by weight ethylene glycol showing thixotropy with raising and lowering of shear (RPM) and an increase in viscosity with increased water content from 0% water to 2% water, 4% water and 6% water; and substantial increase in viscosity when the gel is heated to 85.degree. C. before cooling to 24.degree. C. to measure viscosity (FIG. 13);

FIG. 14 is a graph of composition viscosity at 24.degree. C. of compositions containing 10% by weight Na bentonite:PVP complex (4:1 weight ratio) mixed with water at about 8% to about 28% water and about 72% by weight to about 92% by weight ethanol (water plus ethanol=100%) showing an increase in viscosity with added water between about 8% water and about 20% water by weight and a decrease in viscosity with more than about 20% by weight water;

FIGS. 15 and 16 are graphs of composition viscosity at 24.degree. C. of compositions of varied percentages of water and propylene glycol at various loadings between about 1.25% by weight and about 10% by weight of a complex of Na bentonite clay:PVP (4:1 clay:PVP weight ratio) showing the change in viscosity at various H.sub.2 O percentages (H.sub.2 O plus propylene glycol=100%) and at various clay:PVP complex loadings; and

FIG. 17 is a graph of composition viscosity at 24.degree. C. of compositions of varied percentages of water and glycerol at 0-16% by weight water and 84-100% by weight glycerol at 5% by weight and 10% by weight loadings of a complex of Na bentonite clay:PVP (4:1 clay:PVP weight ratio) showing the change in viscosity at various water percentages (H.sub.2 O plus glycerol=100%) at various clay:PVP complex loadings.

DETAILED DESCRIPTION:

1 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

2 To form the intercalated materials useful in admixture with the carriers or solvents in accordance with the present invention, the phyllosilicate should be swelled or intercalated by sorption of an oligomer or polymer that includes an aromatic ring and/or a functionality selected from the group consisting of carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester, sulfate, sulfonate, sulfinate, sulfamate, phosphate, phosphonate, phosphinate, or combinations thereof. In accordance with a preferred embodiment of the present invention, the intercalating composition should include at least about 4% by weight water, up to about 5000% by weight water, based on the dry weight of the phyllosilicate, preferably about 7% to about 100% water, more preferably about 25% to about 50% by weight water, prior to or during contact with the intercalant polymer to achieve sufficient intercalation for exfoliation. Preferably, the phyllosilicate should include at least about 4% by weight water before contact with the intercalating carrier for efficient intercalation. The amount of intercalant polymer in contact with the phyllosilicate from the intercalating composition, for efficient exfoliation, should provide an intercalant polymer/phyllosilicate weight ratio

(based on the dry weight of the phyllosilicate) of at least about 1:20, preferably at least about 3.2:20, and more preferably about 4-14:20, to provide efficient sorption and complexing (intercalation) of the polymer between the platelets of the layered material, e.g., phyllosilicate, (preferably about 16 to about 70 percent by weight intercalant polymer, based on the dry weight of the layered silicate material).

3 The preferred polymer intercalants are water-soluble and are added to the intercalating composition in the form of a solid or liquid (neat or aqueous solution or dispersion, with or without a liquid organic solvent, e.g., alcohol) having an intercalant polymer concentration of at least about 2%, preferably at least about 5% by weight polymer, more preferably at least about 50% to about 100% by weight intercalant polymer in the intercalating composition, based on the dry weight of the layered material, for intercalant polymer sorption. The polymer can be added as a solid with the addition to the layered material/polymer blend of at least about 20% water, preferably at least about 30% water to about 5000% water or more, based on the dry weight of the layered material, with or without another solvent for the intercalant polymer. Preferably about 30% to about 50% water, more preferably about 30% to about 40% by weight water, based on the dry weight of the layered material, is included in the intercalating composition, when extruding or pug milling, so that less water or solvent is sorbed by the intercalate, thereby necessitating less drying energy after intercalation. The intercalant polymer may be introduced into the spaces between every layer, nearly every layer, or at least a predominance of the layers of the layered material such that the subsequently exfoliated platelet particles are preferably, predominantly less than about 5 layers in thickness; more preferably, predominantly about 1 or 2 layers in thickness; and most preferably, predominantly single platelets.

4 Any swellable layered material that sufficiently sorbs the intercalant polymer to increase the interlayer spacing between adjacent phyllosilicate platelets to at least about 5 .ANG., preferably at least about 10 .ANG. (when the phyllosilicate spacing is measured dry--having a maximum of about 5% by weight water) may be used in the practice of this invention. Useful swellable layered materials include phyllosilicates, such as smectite clay minerals, e.g., montmorillonite, particularly sodium montmorillonite; magnesium montmorillonite and/or calcium montmorillonite; nontronite; beidellite; volkonskoite; hectorite; saponite; sauconite; sobockite; stevensite; svinfordite; vermiculite; and the like. Other useful layered materials include micaceous minerals, such as illite and mixed layered illite/smectite minerals, such as rectorite, tarosovite, ledikite and admixtures of illites with the clay minerals named above.

5 Other layered materials having little or no charge on the layers may be useful in this invention provided they can be intercalated with the intercalant polymers to expand their interlayer spacing to at least about 5 .ANG., preferably to at least about 10 .ANG.. Preferred swellable layered materials are phyllosilicates of the 2:1 type having a negative charge on the layers ranging from about 0.15 to about 0.9 charges per formula unit and a commensurate number of exchangeable metal cations in the interlayer spaces. Most preferred layered materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, sobockite, stevensite, and svinfordite.

6 As used herein the "interlayer spacing" refers to the distance between the internal faces of the adjacent dry layers as they are assembled in the layered material before any delamination (exfoliation) takes place. The interlayer spacing is measured when the layered material is "air dry", e.g., contains about 3-10% water, preferably about 3-6% by weight water, based on the dry weight of the layered material. The preferred clay materials generally include interlayer cations such as Na.sup.+, Ca.sup.+2, K.sup.+, Mg.sup.+2, NH.sub.4.sup.+ and the like, including mixtures thereof.

7 The amount of intercalant polymer intercalated into the swellable layered materials useful in this invention, in order that the intercalated layered material platelet surfaces sufficiently complex with the polymer molecules, such that the layered material may be easily exfoliated or delaminated into individual platelets, may vary substantially between about 10% and about 80%, based on the

dry weight of the layered silicate material. In the preferred embodiments of the invention, amounts of polymer intercalants employed, with respect to the dry weight of layered material being intercalated, will preferably range from about 8 grams of intercalant polymer/100 grams of layered material (dry basis), preferably at least about 10 grams of polymer/100 grams of layered material to about 80-90 grams intercalant polymer/100 grams of layered material. More preferred amounts are from about 20 grams intercalant polymer/100 grams of layered material to about 60 grams intercalant polymer/100 grams of layered material (dry basis).

8 The polymer intercalants are introduced into (sorbed within) the interlayer spaces of the layered material in one of two ways. In a preferred method of intercalating, the layered material is intimately mixed, e.g., by extrusion or pug milling, to form an intercalating composition comprising the layered material, in an intercalant polymer or intercalant polymer/water solution, or intercalant polymer, water and an organic solvent. To achieve sufficient intercalation for exfoliation, the layered material/intercalant polymer blend contains at least about 8% by weight, preferably at least about 10% by weight intercalant polymer, based on the dry weight of the layered material. The intercalating carrier (preferably water, with or without an organic solvent) can be added by first solubilizing or dispersing the intercalant polymer in the carrier; or the dry intercalant polymer and relatively dry phyllosilicate (preferably containing at least about 4% by weight water) can be blended and the intercalating carrier added to the blend, or to the phyllosilicate prior to adding the dry intercalant polymer. In every case, it has been found that surprising sorption and complexing of intercalant polymer between platelets is achieved at relatively low loadings of intercalating carrier, especially H.sub.2 O, e.g., at least about 4% by weight water, based on the dry weight of the phyllosilicate. When intercalating the phyllosilicate in slurry form (e.g. 900 pounds water, 100 pounds phyllosillicate, 25 pounds polymer) the amount of water can vary from a preferred minimum of at least about 30% by weight water, with no upper limit to the amount of water in intercalating composition (the phyllosilicate intercalate is easily separated from the intercalating composition).

9 Alternatively, the intercalating carrier, e.g., water, with or without an organic solvent, can be added directly to the phyllosilicate prior to adding the intercalant polymer, either dry or in solution. Sorption of the polymer intercalant molecules may be performed by exposing the layered material to dry or liquid polymer intercalant compositions containing at least about 2% by weight, preferably at least about 5% by weight intercalant polymer, more preferably at least about 50% intercalant polymer, based on the dry weight of the layered material. Sorption may be aided by exposure of the intercalating composition to heat, pressure, ultrasonic cavitation, or microwaves.

10 In accordance with another method of intercalating the intercalant polymer between the platelets of the layered material and exfoliating the intercalate, the layered material, containing at least about 4% by weight water, preferably about 10% to about 15% by weight water, is blended with an aqueous solution of a water-soluble intercalant polymer in a ratio sufficient to provide at least about 8% by weight, preferably at least about 10% by weight intercalant polymer, based on the dry weight of the layered material. The blend then preferably is extruded for faster intercation of the polymer with the layered material.

11 The preferred polymer intercalants are water-soluble, such as polyvinylpyrrolidone (PVP) having a monomeric structure (I) as follows: ##STR1## The water-solubility of PVP can be adjusted according to (1) the degree of hydrolysis of the polyvinylpyrrolidone, and (2) by forming a metal salt of PVP, such as sodium or potassium. PVP can be hydrolyzed to the structure (II): ##STR2## and the PVP, or copolymers of vinylpyrrolidone and a vinyl amide of .gamma.-amine butyric acid, can be intercalated in the salt form, e.g., sodium or potassium polyvinylpyrrolidone polymers. Preferred PVP intercalants, and the following PVP derivatives, should have a weight average molecular weight in the range of about 100 to about 100,000 or more, more preferably about 1,000 to about 40,000.

12 Other suitable water-soluble vinyl polymers include poly(vinyl alcohol) ##STR3## The polyvinyl alcohols function best when they are essentially fully hydrolyzed,

e.g., 5% or less acetyl groups, preferably 1% or less residual acetyl groups. The lower molecular weight PVA's function best, e.g., a weight average molecular weight of about 2,000 to about 10,000, but higher molecular weights also function, e.g., up to about 100,000.

13 The polyacrylic acid polymers and copolymers and partially or fully neutralized salts, e.g., metal salts, are also suitable, having monomer units: ##STR4## and are commercially available as CARBOPOL resins from B. F. Goodrich and PRIMAL resins from Rohm & Haas. Light cross-linking is acceptable, so long as water-solubility is retained. Weight average molecular weights, for the polyacrylic polymers and copolymers described above and below, of about 10,000 or less, e.g., 200-10,000, intercalate more easily, but higher molecular weights up to about 100,000 or more also function.

14 Other water-soluble derivatives of, and substituted, polyacrylic acids also are useful as intercalant polymers in accordance with the present invention, such as poly(methacrylic acid), (PMAA), having a monomeric structure: ##STR5##

15 Similar water-soluble polymers and copolymers that are suitable in accordance with the present invention include poly(methacrylamide), or PMAAm, having a general monomeric structure: ##STR6##

16 Poly(N,N-Dimethylacrylamide) having the general monomeric structure: ##STR7##

17 Poly(N-Isopropylacrylamide), or PIPAAm, having the monomeric structure: ##STR8##

18 Poly(N-acetamidoacrylamide), having a monomeric structure: ##STR9## and Poly(N-acetmidomethacrylamide), having a monomeric structure: ##STR10## Water-soluble copolymers including any one or more of the above-described acrylic polymers also are useful in accordance with the principles of the present invention, including the acrylic interpolymers of polyacrylic acid and poly(methacrylic acid); polyacrylic acid with poly(methacrylamide); and polyacrylic acid with methacrylic acid.

19 Other suitable water-soluble polymers include polyvinyloxazolidone (PVO) and polyvinylmethyloxazolidone (PVMO), having the monomeric structures: ##STR11## Also suitable are polyoxypropylene, polyoxyethylene block polymers that conform to the formulas: ##STR12## wherein x and z are each an integer in the range of about 4 to about 30; and y is an integer in the range of about 4 to about 100, for example Meroxapol 105; Meroxapol 108; Meroxapol 171; Meroxapol 172; Meroxapol 174; Meroxapol 178; Meroxapol 251; Meroxapol 252; Meroxapol 254; Meroxapol 255; Meroxapol 258; Meroxapol 311; Meroxapol 312; and Meroxapol 314.

20 Other suitable water-soluble/water-dispersible intercalant polymers include polyacrylamide and copolymers of acrylamide; acrylamide/sodium acrylate copolymer; acrylate/acrylamide copolymer; acrylate/ammonium methacrylate copolymer; acrylate/diacetoneacrylamide copolymers; acrylic/acrylate copolymers; adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; ammonium acrylate copolymers; ammonium styrene/acrylate copolymers; ammonium vinyl acetate/acrylate copolymers; aminomethanepropanol (AMP) acrylate/diacetoneacrylamide copolymers; aminomethylpropanediol (AMPD) acrylate/diacetoneacrylamide copolymers; butyl benzoic acid/phthalic anhydride/trimethylolethane copolymer; cornstarch/acrylamide/sodium acrylate copolymer; diethylene glycolamine/epichlorohydrin/piperazine copolymer; dodecanedioic acid/cetearyl alcohol/glycol copolymers; ethylene/vinyl alcohol copolymer; ethyl ester of polyethyleneimines, such as hydroxyethyl/PEI-1000 and hydroxyethyl PEI-1500; isopropyl ester of, polyvinyl methacrylate/methacrylic acid (PVM/MA) copolymer; melamine/formaldehyde resin; methacryloyl ethyl betaine/methacrylate copolymers; methoxy PEG-22/dodecyl glycol copolymer; octadecene/maleic anhydride copolymer; octylacrylamide/acrylate/butylaminoethyl methacrylate copolymers; octylacrylamide/acrylate copolymers; polyethylene glycol (PEG)/dodecyl glycol copolymers; polyvinylimines, such as, PEI-7; PEI-15; PEI-30; PEI-45; PEI-275; PEI-700; PEI-1000; PEI-1500; and PEI-2500; phthalic anhydride/glycerin/glycidyl decanoate copolymer; metal salts of acrylic and polyacrylic acid; polyaminopropyl biguanide; polymeric quaternary ammonium salts, such as polyquaternium-1;

polyquaternium-2; polyquaternium-4; polyquaternium-5; polyquaternium-6; polyquaternium-7; polyquaternium-8; polyquaternium-9; polyquaternium-10; polyquaternium-11; polyquaternium-12; polyquaternium-13; polyquaternium-14; and polyquaternium-15; polyvinyl imidazolinium acetate; potassium polyacrylate; sodium polyacrylate; metal salts of PVM/MA copolymers, e.g. Li, K, Na, Ru, Ce salts; polyvinylpyrrolidone (PVP)/eicosene copolymers; PVP/ethyl methacrylate/methacrylic acid copolymer; PVP/hexadecene copolymer; polyvinylpyrrolidone/vinyl acetate (PVP/VA) copolymer; PVP/vinyl acetate/itaconic acid copolymer; sodium acrylate/vinyl alcohol copolymers; sodium C.sub.4 -C.sub.12, and other metal salts of olefin/maleic acid copolymers; sodium polymethacrylate; sodium polystyrene sulfonate; sodium styrene/acrylate/PEG-10 dimaleate copolymer; water-soluble esters and ethers of cellulose; sodium styrene/PEG-10 maleate/nonoxynol-10 maleate/acrylate copolymer; starch/acrylate/acrylamide copolymers; styrene/acrylamide copolymer; styrene/acrylate/ammonium methacrylate copolymer; styrene/maleic anhydride copolymer; styrene/PVO copolymer; sucrose benzoate/sucrose acetate isobutyrate/butyl benzyl phthalate copolymer; sucrose benzoate/sucrose acetate isobutyrate/butyl benzylphthalate/methyl methacrylate copolymer; urea/formaldehyde prepolymers; urea/melamine/formaldehyde prepolymers; vinyl acetate/crotonic acid copolymers; and vinyl alcohol copolymers.

21 Other water-soluble polymeric polyols and polyhydric alcohols, such as polysaccharides, also are suitable as polymer intercalants.

22 The amount of intercalated and/or exfoliated layered material included in the liquid carrier or solvent compositions to form the viscous compositions suitable to deliver the carrier or some carrier-dissolved or carrier-dispersed active material, such as a pharmaceutical, may vary widely depending on the intended use and desired viscosity of the composition. For example, relatively higher amounts of intercalates, i.e., from about 10% to about 30% by weight of the total composition, are used in forming solvent gels having extremely high viscosities, e.g., 5,000 to 5,000,000 centipoises. Extremely high viscosities, however, also can be achieved with a relatively small concentration of intercalates and/or exfoliates thereof, e.g., 0.1% to 5% by weight, by adjusting the pH of the composition in the range of about 0-6 or about 10-14 and/or by heating the composition above room temperature, e.g., in the range of about 25.degree. C. to about 200.degree. C., preferably about 75.degree. C. to about 100.degree. C. It is preferred that the intercalate or platelet loading be less than about 10% by weight of the composition. Intercalate or platelet particle loadings within the range of about 0.01% to about 40% by weight, preferably about 0.05% to about 20%, more preferably about 0.5% to about 10% of the total weight of the composition significantly increases the viscosity of the composition. In general, the amount of intercalate and/or platelet particles incorporated into the carrier/solvent is less than about 20% by weight of the total composition, and preferably from about 0.05% to about 20% by weight of the composition, more preferably from about 0.01% to about 10% by weight of the composition, and most preferably from about 0.01% to about 5%, based on the total weight of the composition.

23 In accordance with an important feature of the present invention, the intercalate and/or platelet/carrier compositions of the present invention can be manufactured in a concentrated form, e.g., as a master gel, e.g., having about 10-90%, preferably about 20-80% intercalate and/or exfoliated platelets of layered material and about 10-90%, preferably about 20-80% carrier/solvent. The master gel can be later diluted and mixed with additional carrier or solvent to reduce the viscosity of the composition to a desired level.

24 The intercalates, and/or exfoliates thereof, are mixed with a carrier or solvent to produce viscous compositions of the carrier or solvent optionally including one or more active compounds, such as an antiperspirant compound, dissolved or dispersed in the carrier or solvent.

25 In accordance with an important feature of the present invention, a wide variety of topically-active compounds can be incorporated into a stable composition of the present invention. Such topically active compositions include cosmetic, industrial, and medicinal compounds that act upon contact with the skin or hair, or are used to adjust rheology of industrial greases and the like. In accordance

with another important feature of the present invention, a topically-active compound can be solubilized in the composition of the present invention or can be homogeneously dispersed throughout the composition as an insoluble, particulate material. In either case topically-effective compositions of the present invention are resistant to composition separation and effectively apply the topically-active compound to the skin or hair. If required for stability, a surfactant can be included in the composition, such as any disclosed in Laughlin, et al. U.S. Pat. No. 3,929,678, hereby incorporated by reference. In general, the topically-effective compositions of the present invention demonstrate essentially no phase separation if the topically-active compound is solubilized in the compositions. Furthermore, if the topically-active compound is insoluble in the composition, the composition demonstrates essentially no phase separation.

26 The topically-active compounds can be a cosmetically-active compound, a medically-active compound or any other compound that is useful upon application to the skin or hair. Such topically-active compounds include, for example, antiperspirants, antidandruff agents, antibacterial compounds, antifungal compounds, anti-inflammatory compounds, topical anesthetics, sunscreens and other cosmetic and medical topically-effective compounds.

27 Therefore, in accordance with an important feature of the present invention, the stable topically-effective composition can include any of the generally-known antiperspirant compounds such as finely-divided solid astringent salts, for example, aluminum chlorohydrate, aluminum chlorohydrox, zirconium chlorohydrate, and complexes of aluminum chlorohydrate with zirconyl chloride or zirconyl hydroxychloride. In general, the amount of the antiperspirant compound, such as aluminum zirconium tetrachlorohydrex glycine in the composition can range from about 0.01% to about 50%, and preferably from about 0.1% to about 30%, by weight of the total composition.

28 Other topically-active compounds can be included in the compositions of the present invention in an amount sufficient to perform their intended function. For example, zinc oxide, titanium dioxide or similar compounds can be included if the composition is intended to be a sunscreen. Similarly, topically-active drugs, like antifungal compounds; antibacterial compounds; anti-inflammatory compounds; topical anesthetics; skin rash, skin disease and dermatitis medications; and anti-itch and irritation-reducing compounds can be included in the compositions of the present invention. For example, analgesics such as benzocaine, dyclonine hydrochloride, aloe vera and the like; anesthetics such as butamben picrate, lidocaine hydrochloride, zylocaine and the like; antibacterials and antiseptics, such as povidone-iodine, polymyxin b sulfate-bactracin, zinc-neomycin sulfate-hydrocortisone, chloramphenicol, methylbenzethonium chloride, and erythromycin and the like; antiparasitics, such as lindane; deodorants, such as chlorophyllin copper complex, aluminum chloride, aluminum chloride hexahydrate, and methylbenzethonium chloride; essentially all dermatologicals, like acne preparations, such as benzoyl peroxide, erythromycinbenzoyl peroxide, clindamycin phosphate, 5,7-dichloro-8-hydroxyquinoline, and the like; anti-inflammatory agents, such as alclometasone dipropionate, betamethasone valerate, and the like; burn relief ointments, such as o-amino-p-toluenesulfonamide monoacetate and the like; depigmenting agents, such as monobenzone; dermatitis relief agents, such as the active steroids amcinonide, diflorasone diacetate, hydrocortisone, and the like; diaper rash relief agents, such as methylbenzethonium chloride and the like; emollients and moisturizers, such as mineral oil, PEG-4 dilaurate, lanolin oil, petrolatum, mineral wax and the like; fungicides, such as butocouazole nitrate, haloprogin, clotrimazole, and the like; herpes treatment drugs, such as 9-[(2-hydroxyethoxy)methyl]guanine; pruritic medications, such as alclometasone dipropionate, betamethasone valerate, isopropyl myristate MSD, and the like; psoriasis, seborrhea and scabicide agents, such as anthralin, methoxsalen, coal tar and the like; sunscreens, such as octyl p-(dimethylamino)benzoate, octyl methoxycinnamate, oxybenzone and the like; steroids, such as 2-(acetyloxy)-9-fluoro-1',2',3',4'-tetrahydro-11-hydroxypregna-1,4-dieno[1 6,17-b]naphthalene-3,20-dione, and 21-chloro-9-fluoro-1',2',3',4'-tetrahydro-11b-hydroxypregna-1,4-dieno[16z, 17-b]naphthalene-3,20-dione. Any other medication capable of topical administration also can be incorporated in composition of the present invention in

an amount sufficient to perform its intended function.

29 Eventual exfoliation of the intercalated layered material should provide delamination of at least about 90% by weight of the intercalated material to provide a more viscous composition comprising a carrier or solvent having polymer-complexed platelet particles substantially homogeneously dispersed therein. Some intercalates require a shear rate that is greater than about 10 sec.sup.-1 for such relatively thorough exfoliation. Other intercalates exfoliate naturally or by heating, or by applying low pressure, e.g., 0.5 to 60 atmospheres above ambient, with or without heating. The upper limit for the shear rate is not critical. In the particularly preferred embodiments of the invention, when shear is employed for exfoliation, the shear rate is from greater than about 10 sec.sup.-1 to about 20,000 sec.sup.-1, and in the more preferred embodiments of the invention the shear rate is from about 100 sec.sup.-1 to about 10,000 sec.sup.-1.

30 When shear is employed for exfoliation, any method which can be used to apply a shear to the intercalant/carrier composition can be used. The shearing action can be provided by any appropriate method, as for example by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics, all known in the art. In particularly useful procedures, the composition is sheared by mechanical methods in which the intercalate, with or without the carrier or solvent, is sheared by use of mechanical means, such as stirrers, Banbury.RTM. type mixers, Brabender.RTM. type mixers, long continuous mixers, and extruders. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the composition causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic techniques in which cavitation or resonant vibrations which cause portions of the composition to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing are merely representative of useful methods, and any method known in the art for shearing intercalates may be used.

31 Mechanical shearing methods may be employed such as by extrusion, injection molding machines, Banbury.RTM. type mixers, Brabender.RTM. type mixers and the like. Shearing also can be achieved by introducing the layered material and intercalant polymer at one end of an extruder (single or double screw) and receiving the sheared material at the other end of the extruder. The temperature of the layered material/intercalant polymer composition, the length of the extruder, residence time of the composition in the extruder and the design of the extruder (single screw, twin screw, number of flights per unit length, channel depth, flight clearance, mixing zone, etc.) are several variables which control the amount of shear to be applied for exfoliation.

32 Exfoliation should be sufficiently thorough to provide at least about 80% by weight, preferably at least about 85% by weight, more preferably at least about 90% by weight, and most preferably at least about 95% by weight delamination of the layers to form individual platelet particles that can be substantially homogeneously dispersed in the carrier or solvent. As formed by this process, the platelet particles dispersed in the carrier or solvent have the thickness of the individual layers plus one to five monolayer thicknesses of complexed polymer, or small multiples less than about 10, preferably less than about 5 and more preferably less than about 3 of the layers, and still more preferably 1 or 2 layers. In the preferred embodiments of this invention, intercalation and delamination of every interlayer space is complete so that all or substantially all individual layers delaminate one from the other to form separate platelet particles for admixture with the carrier or solvent. The compositions can include the layered material as all intercalate, completely without exfoliation, initially to provide relatively low viscosities for transportation and pumping until it is desired to increase viscosity via easy exfoliation. In cases where intercalation is incomplete between some layers, those layers will not delaminate in the carrier or solvent, and will form platelet particles comprising those layers in a coplanar aggregate.

33 The effect of adding into a carrier or solvent the nanoscale particulate dispersed platelet particles, derived from the intercalates formed in accordance with the present invention, typically is a substantial increase in viscosity of the carrier or solvent.

34 The following specific clay:polymer complex preparations are presented to more particularly illustrate the invention and are not to be construed as limitations thereon.

35 Preparation of Clay--PVP Complexes (Intercalates)

36 Materials:

37 Clay--sodium montmorillonite;

38 PVP--molecular weights of 10,000 and 40,000.

39 To prepare Clay (sodium montmorillonite)--PVP complexes (intercalates) we used three different processes for polymer intercalation:

40 1. Mixture of the 2% PVP/water solution with the 2% clay/water suspension in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the dry weight of the clay.

41 2. Dry clay powder (about 8% by weight moisture) was gradually added to the 2% PVP/water solution in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the dry weight of the clay.

42 3. Dry PVP was mixed with dry clay, the mixture was hydrated with 25-50%, preferably 35%-40% by weight water, based on the dry weight of the clay, and then extruded.

43 Mixtures 1 and 2 were agitated at room temperature during 4 hours.

44 The weight ratio Clay:PVP was changed from 90:10 to 20:80.

45 These experiments show that all methods of preparation yielded the Clay--PVP complexes (intercalates), and the results of the intercalation do not depend on the method of preparation (1, 2, or 3) or molecular weight of the intercalant polymer (PVP), but do depend on the ratio of clay:PVP in the intercalating composition. In Table 1 the results of the X-ray diffraction for Clay--PVP complexes with different ratios of components are demonstrated. The plot of these data is shown in FIG. 1. From these data (Table 1, FIG. 1) one can see the step character of intercalation while the polymer is being sorbed in the interlayer space between adjacent platelets of the montmorillonite clay. There are increasing d(001) values from 12 .ANG. for clay with no PVP sorbed to 24-25 .ANG. spacing between adjacent platelets with sorption of 20-30% PVP. The next step to 30-32 .ANG. spacing occurs when the sorbed PVP content is increased to 40-60%. Further increasing the sorbed PVP content to 70-80% increases the d(001) values to 40-42 .ANG.. There are d(002) reflexes together with d(001) reflexes in X-ray patterns of all complexes obtained (Table 1, FIG. 1). This indicates the regularity of Clay--PVP complex structures.

TABLE 1

	PVP, %*	d (001), .ANG.	d (002), .ANG.
1	0.0	12.4	6.2
2	10.0	17.5	8.6
3	20.0	24.0	11.4

4	30.0	25.0	12.0
5	40.0	30.0	15.2
6	45.0	31.0	15.2
7	50.0	30.0	15.5
8	55.0	32.0	16.5
9	60.0	34.0	17.0
10	70.0	40.0	21.0
11	80.0	42.0	21.0

*Percent by weight, based on the dry weight of the clay plus polymer.

46 Preparation of Clay--PVA Complexes (Intercalates)

47 Materials:

48 Clay--sodium montmorillonite;

49 PVOH--degree of hydrolysis 75-99%, molecular weight of 10,000.

50 To prepare Clay (sodium montmorillonite)--PVOH complexes (intercalates) we provided three different processes for polymer intercalation:

51 1. Mixture of the 2% PVOH/water solution with the 2% clay/water suspension in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the dry weight of the clay.

52 2. Dry clay powder was gradually added to the 2% PVOH/water solution in a ratio sufficient to provide a polymer concentration of at least about 8% by weight, preferably at least about 10% by weight, based on the weight of the clay.

53 3. Dry clay was moisturized with PVOH/water solution to a moisture content of 25%-80%, preferably about 35%-40% water, and then extruded.

54 The mixtures 1 and 2 were agitated at room temperature during 4 hours.

55 The weight ratio Clay:PVOH was changed from 80:20 to 20:80.

56 Some of the exfoliates were studied by X-ray diffraction. These experiments show that all methods of preparation yielded the composite Clay--PVOH complexes (intercalates), and the results of the intercalation do not depend on the method of preparation (1, 2, or 3), or molecular weight of the intercalant polymer (PVOH), or degree of hydrolysis, but do depend on the ratio of clay:PVOH in the intercalating composition. In Table 2 the results of the X-ray diffraction for Clay--PVOH complexes with different ratios of components are demonstrated. The plot of these data is shown in FIG. 2. From these data (Table 2, FIG. 2) one can see the step character of increasing d(001) values from 12 .ANG. for clay with no sorbed PVOH to 22-25 .ANG. spacing between adjacent platelets with sorption of 20-30% PVOH. The next step to 30-33 .ANG. occurs when the sorbed PVOH content increases to 35-50%. A further increase of the sorbed PVOH content to 60-80% increases the d(001) values to 40-45 .ANG..

57 Heating of samples at 120.degree. C. during 4 hours insignificantly changed the d(001) values (Table 2, FIG. 2).

TABLE 2

	PVOH %*	d (001), .ANG.	d (001), .ANG. 120.degree. C.
1	0.0	12.4	9.6
2	10.0	17.0	16.8

3	20.0	23.0	22.0
4	30.0	25.0	24.0
5	35.0	32.0	32.0
6	40.0	31.0	30.0
7	45.0	33.0	32.0
8	50.0	32.0	32.0
9	60.0	42.0	42.0
10	70.0	44.0	42.0
11	80.0	45.0	44.0

*Percent by weight, based on the dry weight of the clay plus PVOH.

58 The graphs of FIGS. 3 to 5 are x-ray diffraction patterns of blends of different water-soluble polymers with sodium bentonite clay. The pattern of FIGS. 3 and 4 are taken from intercalated clay 20% by weight polyvinylpyrrolidone (weight average molecular weight=10,000 for FIG. 3; 40,000 for FIG. 4) and 80% by weight sodium bentonite clay. The blends were formed by mixing the PVP and clay from a 2% solution of PVP and a 2% dispersion of sodium bentonite in a 1:4 ratio, respectively. As shown, the PVP:clay complexed since no d(001) smectite peak appears at about 12.4 .ANG.. Similar results are shown for 20% polyvinyl alcohol, 80% sodium bentonite, as shown in FIG. 5, blended in the same way and in the same ratio. The d(001) peak of non-exfoliated (layered) sodium bentonite clay appears at about 12.4 .ANG., as shown in the x-ray diffraction pattern for sodium bentonite clay (containing about 10% by weight water) in the lower x-ray diffraction patterns of FIGS. 6 and 7. The graphs of FIG. 6 are x-ray diffraction patterns of sodium bentonite clay (montmorillonite) and a PVP:clay complex that was obtained by extrusion of a blend of 20% by weight polyvinylpyrrolidone (molecular weight 10,000) and 80% by weight sodium bentonite clay (containing a crystobalite impurity, having a d-spacing of about 4.05 .ANG.) with 35% water based on the weight of dry clay plus polymer. As shown in FIG. 6, the PVP clay complexed since no d(001) smectite peak appears at about 12.4 .ANG.. There are basal spacings with a d(001) peak of PVP:clay complex at about 24 .ANG. and d(002) peak of PVP:clay complex at about 12 .ANG., that shows close to regular structure of this intercalated composite with a PVP:clay ratio equal to 1:4. The graphs of FIG. 7 are x-ray diffraction patterns of sodium bentonite clay (montmorillonite) and PVP:clay complex that was obtained by extrusion of blend of 50% by weight polyvinylpyrrolidone (molecular weight 10,000) and 50% of sodium bentonite clay (containing a crystobalite impurity, having d-spacing of about 4.05 .ANG.) with 35% water based on the weight of dry clay plus polymer. As shown in FIG. 7, the PVP:clay complexed since no d(001) smectite peak appears at about 12.4 .ANG.. There are basil spacings with a d(001) peak of the PVP:clay complex at about 32 .ANG. and a d(002) peak of PVP:clay complex at about 16 .ANG. that shows close to regular structure of this intercalated composite with a PVP:clay ratio equal to 1:1. When mechanical blends of powdered sodium bentonite clay (containing about 10% by weight water) and powdered polyvinylpyrrolidone (PVP) polymer were mixed with water (about 75% by weight water), the polymer was intercalated between the bentonite clay platelets, and an exothermic reaction occurred that, it is theorized, resulted from the polymer being bonded to the internal faces of the clay platelets sufficiently for exfoliation of the intercalated clay.

59 It should be noted, also, that exfoliation did not occur unless the bentonite clay included water in an amount of at least about 4% by weight, based on the dry weight of the clay, preferably at least about 10% by weight water. The water can be included in the clay as received, or can be added to the clay prior to or during intercalant polymer contact.

60 It should also be noted that the exfoliation occurred without shearing--the layered clay exfoliated naturally after sufficient intercalation of polymer between the platelets of the layered bentonite--whether the intercalate was achieved by using sufficient water, e.g., at least about 20% by weight, preferably about 30% to about 100% by weight, or higher, based on the dry weight of the clay, for sufficient migration of the polymer into the interlayer spaces, and preferably also by extruding. When intercalating in a phyllosilicate slurry, it has been found that at least about 65% by weight water, based on the total weight of the

intercalating composition, provides easier mixing and faster migration of the polymer into the spaces between platelets.

61 The x-ray diffraction pattern of FIG. 8 shows that at a ratio of 80% PVP, 20% clay, the periodicity of the intercalated composite, with a PVP clay ratio equal to 4:1, is increased to about 41 .ANG..

62 A number of compositions were prepared containing intercalates (complexes) formed by contacting sodium bentonite clay with an intercalating composition. The intercalating composition contained clay, water and a water-soluble polymer. Sufficient sodium bentonite clay was added to the intercalating composition to provide a preferred weight ratio of dry clay/polymer of 4:1 (80% by weight clay/20% by weight polymer) with sufficient water such that the intercalating composition and clay contained 35-40% by weight water for effective extrusion of the composition through die openings of an extruder. Similarly, the polymer and water can be mixed with clay to complex (intercalate) the polymer to the platelet surfaces between adjacent clay platelets.

63 The complex (intercalate) was then combined with various organic liquids (with and without water) to determine the effect of intercalate loading as well as temperature, pH and water content of the intercalating composition on the viscosity of the liquid by the addition of the intercalate or exfoliate thereof. For the composition shown in FIGS. 9-14, every clay-PVP (polyvinylpyrrolidone) complex was an extruded blend having a weight ratio of clay:PVP of 4:1 containing 35-40% by weight water, based on the dry weight of the clay plus polymer. The complexes (intercalates and/or exfoliates) formed by extrusion were admixed, at various complex percentages, with the designated percentages of organic liquid (sometimes also with water) and the viscosity measured using a Brookfield viscometer, spindle #4, unless otherwise noted.

64 As shown in the graph of FIG. 9, a composition consisting of 10% by weight of an extruded complex of 80% by weight sodium bentonite clay and 20% by weight polyvinylpyrrolidone (extruded using 38% water, based on the dry weight of the clay plus polymer, and then dried) was combined with 6% water and 84% glycerol. The composition was mixed to form a homegeneous composition and sometimes heated to form a more viscous gel before cooling to room temperature (24.degree. C.) to measure the viscosity. As shown in FIG. 9, mixing 10% by weight clay:PVP intercalate into 84% glycerol, and 6% water resulted in a viscosity of 2,000-3,000 centipoises and heating the composition to gelation resulted in viscosities of about 3,500-4,000 centipoises (80.degree. C.) and 7,000-8,000 centipoises (100.degree. C.)--all viscosities being measured at 24.degree. C.

65 As shown in FIG. 10, when the intercalate/water/glycerol compositions of FIG. 9 were heated to 145.degree. C. and then cooled to room temperature, the viscosity of the 10% intercalate/6% H.sub.2 O/84% glycerol composition was increased to about 200,000 to about 600,000 centipoises.

66 FIG. 11 shows compositions similar to those of FIGS. 9 and 10 at two different loadings (5% by weight and 10% by weight) of the clay:PVP complex (again, a 4:1 weight ratio of sodium bentonite to polyvinylpyrrolidone extruded with 38% water and then dried to about 3%-10% water, preferably about 4% to 6% water) with glycerol and water, with varied amounts of water. The compositions were gelled by heating to 140.degree. C. and the compositions were cooled to room temperature (24.degree. C.) before the viscosity was measured. As shown in FIG. 11, for a 5% loading of the intercalate, an increase in water percentage up to about 5% by weight causes an increase in viscosity; for a 10% intercalate loading, an increase in water percentage up to about 8% by weight increases the viscosity of the intercalate/glycerol/water composition--with viscosities of about 500,000 centipoises to about 3,000,000 centipoises being achieved.

67 FIG. 12 is a graph showing viscosity measured at room temperature (24.degree. C.), of compositions containing 5% by weight of the sodium bentonite clay:PVP complex (intercalate) admixed with 0-6% by weight water and 89-95% by weight ethylene glycol, without heating. As shown in FIG. 12, the addition of up to about 6% by weight water increases the viscosity of the intercalate/ethylene glycol

composition-(without heating) from less than 1,000 centipoises to more than 9,000 centipoises. The same compositions were heated to 85.degree. C. and the viscosity measured (after cooling to room temperature). The effect of temperature (85.degree. C.) is quite dramatic, as shown in FIG. 13, increasing the viscosity to well over 100,000 centipoises, with the addition of about 2% by weight water, and increasing viscosity, substantially, without water as well.

68 FIG. 14 is a graph showing viscosity, again measured at room temperature (24.degree. C.) of an unheated mixture of 10% by weight sodium bentonite clay:PVP complex (intercalate), with the remainder being varied percentages of ethanol and water. As shown in FIG. 14, for ethanol, the addition of up to about 20% by weight water (70% ethanol, 10% clay:PVP complex) increases the viscosity of the composition from well below 400,000 centipoises to about 1,000,000 centipoises, even without heating.

69 Various other organic liquids were admixed with clay:polymer intercalates at varied percentages of intercalate and varied percentages of water. All experiments used a 4:1 weight ratio of sodium bentonite clay to polyvinylpyrrolidone either mixed with a water slurry of the clay and polymer at 5-80% water--Technique #1) and then dried; or extruded with 35-38% water and then dried (Technique #2). The results are shown in the following examples:

70 EXAMPLE 1

2-PROPANOL WITH 10%-4:1 COMPLEX (CLAY:PVP)
10%-4:1 Complex (20 grams) 27%-Water (54 grams)
63%-2-Propanol (126 grams) TECHNIQUE #1
Spindle: #1

RPM	3	6	12
Viscosity (cps)			
	762	393	234

71 EXAMPLE 2

8% Water (16 grams) 5%-4:1 Complex (10 grams)
87% Propylene Glycol (174 grams) TECHNIQUE #1
Spindle: #4 Was heated to 160.degree. C.

RPM	3	6	12
Viscosity (cps)			
	23,800	11,700	7,700

72 EXAMPLE 3

8% Water (16 grams) 5%-4:1 Complex (10 grams)
87% Propylene Glycol (174 grams) TECHNIQUE #2
Spindle: #4 Was heated to 160.degree. C.

RPM	3	6	12
Viscosity (cps)			
	23,600	9,100	5,600

73 EXAMPLE 4

8% Water (16 grams) 10%-4:1 Complex (20 grams) 82% Propylene Glycol (164 grams) TECHNIQUE #1 Spindle: #4 Was heated to 115-120.degree. C.			
RPM	3	6	12
Viscosity (cps)			
	21,400	11,700	7,350

74 EXAMPLE 5

8% Water (16 grams) 10%-4:1 Complex (20 grams) 82% Propylene Glycol (164 grams) TECHNIQUE #2 Spindle: #4 Was heated to 115-120.degree. C.			
RPM	3	6	12
Viscosity (cps)			
	19,000	10,600	6,950

75 Propylene glycol, glycerol, propanol, acetone, and anhydrous alcohol were mixed with varied percentages of sodium bentonite clay:PVP complexes, either slurried or extruded with water and then dried, and varied percentages of water, as shown in the following Examples.

76 EXAMPLE 6

Propylene Glycol Gel % of Complex	% of Water	Syneresis
20	8	None

77 EXAMPLE 7

Propylene Glycol Gel % of Complex	% of Water	Syneresis
15	8	None
15	24	None

78 EXAMPLE 8

Propylene Glycol Gel % of Complex	% of Water	Syneresis
10	4	None
10	6	None
10	8	None
10	16	None
10	24	None

79 EXAMPLE 9

Propylene Glycol Gel % of Complex	% of Water	Syneresis
5	4	Very Little
5	8	Very Little
5	16	Very Little
5	24	None
5	30	None

80 EXAMPLE 10

Propylene Glycol Gel % of Complex	% of Water	Syneresis
2.5	4	Very Little
2.5	8	None
2.5	12	None
2.5	16	None
2.5	24	None

81 EXAMPLE 11

Glycerol Gel % of Complex	% of Water	Syneresis
10	0	None
10	4	None
10	8	None
10	16	None

82 EXAMPLE 12

Glycerol Gel % of Complex	% of Water	Syneresis
5	0	None
5	2	None
5	4	None
5	8	None

83 EXAMPLE 13

Ethylene Glycol Gel % of Complex	% of Water	Syneresis
10	8	None
10	16	None

84 EXAMPLE 14

Ethylene Glycol Gel % of Complex	% of Water	Syneresis
5	0	Very Little
5	2	None
5	4	None
5	6	None

85 EXAMPLE 15

Alcohol, Anydrous Reagent - 9401-03 % of Complex	% of Water	Syneresis
10	4	Very Much
10	8	Yes
10	16	None

86 EXAMPLE 16

1,4 Butane Diol Gel % of Complex	% of Water	Syneresis
10	4	None

87 EXAMPLE 17

1,4 Butane Diol Gel % of Complex	% of Water	Syneresis
5	4	Very Little
5	8	None
5	16	None

88 EXAMPLE 18

1-Propanol Gel % of Complex	% of Water	Syneresis
10	8	Yes
10	27	Yes
10	45	Yes
10	50	None

89 EXAMPLE 19

Acetone Gel % of Complex	% of Water	Syneresis
20	40	None

90 EXAMPLE 20

Acetone Gel % of Complex	% of Water	Syneresis
10	16	Yes

10	45	None
10	50	None

91 EXAMPLE 21

10% Complex, 8% Water, 72% Propylene Glycol (Master Gel)
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)			
	464,000	306,000	162,800

92 EXAMPLE 22

27.5% Master Gel of Example 21
65% Silicone Oil, 0.75% Abil*, 6.75% Water
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)			
	1,630,000	EEE**	EEE**

* Abil: Amino silane surfactant from Huls America
**EEE -- Exceeded capacity of viscometer

93 EXAMPLE 23

15% Complex, 24% Water, 61% Propylene Glycol (Master Gel)
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)			
	456,000	278,000	142,400

94 EXAMPLE 24

27.5% Master Gell of Example 23
65% Silicone Oil, 0.75% Abil, 6.75% Water
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)			
	1,000,000	625,000	361,200

95 EXAMPLE 25

15% Complex, 8% Water, 77% Propylene Glycol (Master Gel)
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)	168,000	63,000	40,800

96 EXAMPLE 26

27.5% Master Gel of Example 25
65% Silicone Oil, 0.75% Abil, 6.75% Water
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)	1,630,000	981,000	EEE*

*EEE -- Exceeded capacity of ter

97 EXAMPLE 27

10% Complex, 0% Water, 90% Glycerol (Master Gel)
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)	EEE*	EEE*	EEE*

*EEE -- Exceeded Capacity of viscometer

98 EXAMPLE 28

10% Complex, 4% Water, 85% Glycerol (Master Gel)
Spindle: #4

RPM	0.3	0.6	1.5
Viscosity (cps)	240,000	137,000	114,000

99 EXAMPLE 29

37.5% - Master Gel of Example 27,

51% Silicone Oil, 1.0% Abil, 11% Water Spindle: #4			
RPM	0.3	0.6	1.5
Viscosity (cps)	376,000	308,000	180,400

100 EXAMPLE 30

37.5% - Master Gel of Example 28, 51% Silicone Oil, 1.0% Abil, 11% Water Spindle: #4			
RPM	0.3	0.6	1.5
Viscosity (cps)	512,000	371,000	201,600

101 EXAMPLE 31

37.5% - Master Gel of Example 28, 55% Silicone Oil, 1% Abil, 6.5% Water Spindle: #4			
RPM	0.3	0.6	1.5
Viscosity (cps)	1,164,000	699,000	EEE*

*EEE -- Exceeded capacity of viscometer

102 EXAMPLE 32

34% Master Gel of Example 28, 60% Silicone Oil, 1.0% Abil, 5% Water Spindle: #4			
RPM	0.3	0.6	1.5
Viscosity (cps)	EEE*	EEE*	EEE*

*EEE -- Exceeded capacity of viscometer

103 EXAMPLE 33

10% Complex (20 grams), 4% Water (8 grams),
91% Propylene Glycol (182 grams)
Spindle: #4

RPM	3	6	12
Viscosity (cps)	16,200	10,500	7,550

104 EXAMPLE 34

10% Complex (20 grams), 6% Water (12 grams,)
84% Propylene Glycol (168 grams)
Spindle: #4

RPM	3	6	12
Viscosity (cps)	22,200	15,300	12,000

105 EXAMPLE 35

10% Complex (20 grams), 8% Water (16 grams),
82% Propylene Glycol (164 grams)
Spindle: #4

RPM	3	6	12
Viscosity (cps)	14,400	12,100	9,400

106 EXAMPLE 36

10% Complex (20 grams), 16% Water (32 grams),
74% Propylene Glycol (148 grams)
Spindle: #4

RPM	3	6	12
Viscosity (cps)	12,000	10,600	7,500

107 EXAMPLE 37

10% Complex (20 grams), 24% Water (48 grams),
66% Propylene Glycol (132 grams)
Spindle: #4

RPM	3	6	12
Viscosity (cps)	22,400	13,100	8,650

108 EXAMPLE 38

4% Water (8 grams), 1.25% Complex 4:1 (2.5 grams),
94.75% Propylene Glycol (189.5 grams) - Was heated to 170.degree. C.
Spindle: #2

RPM	3	6	12
Viscosity (cps)	290	285	227.5

109 EXAMPLE 39

8% Water (16 grams), 1.25% Complex 4:1 (2.5 grams),
90.75% Propylene Glycol (181.5 grams) - Was heated to 160-165.degree. C.
Spindle: #2

RPM	3	6	12
Viscosity (cps)	510	420	385

110 EXAMPLE 40

12% Water (24 grams), 1.25% Complex 4:1 (2.5 grams),
86.75% Propylene Glycol (173.5 grams) - Was heated to 165-170.degree. C.
Spindle: #2

RPM	3	6	12
Viscosity (cps)	4,500	3,135	1,897.5

111 EXAMPLE 41

16% Water (32 grams), 1.25% Complex 4:1 (2.5 grams),
82.75% Propylene Glycol (165.5 grams) - Was geated to 170.degree. C.
Spindle: #2

RPM	3	6	12
Viscosity (cps)	5,370	3,350	1,970

112 EXAMPLE 42

4% Water (8 grams), 5% Complex (10 grams),
91% Propylene Glycol (182 grams) - Heated to 110.degree. C. - From 110 to 155.degree. C. took 15 min. - Max. temp. = 160.degree. C.
Spindle: #2

RPM	12	30	60
Viscosity (cps)	112.5	94.0	91.5

113 EXAMPLE 43

4% Water (8 grams), 5% Complex (10 grams),
91% Propylene Glycol (182 grams) - Heated to 110.degree. C. - From 110 to 155.degree. C. took 15 min. - Max. temp. = 160.degree. C.
Spindle: #4

RPM	1.5	3	6	12
Viscosity (cps)	78,000	36,600	21,200	11,950

114 EXAMPLE 44

8% Water (16 grams), 5% Complex (10 grams),
87% Propylene Glycol (174 grams) - Heated to 150.degree. C. - From 110 to 150.degree. C. took 20 min. - Max. temp. = 150.degree. C.
Spindle: #2

RPM	12	30	60
Viscosity (cps)	145.0	130.0	120.5

115 EXAMPLE 45

16% Water (32 grams), 5% Complex (10 grams),
79% Propylene Glycol (158 grams) - Heated to 145-150.degree. C. - From 110 to 150.degree. C. took 19 min. - Max. temp. = 150.degree. C.
Spindle: #2

RPM	30	60
Viscosity (cps)	98.0	102.5

116 EXAMPLE 46

16% Water (32 grams), 5% Complex (10 grams),
79% Propylene Glycol (158 grams) - Heated to 145-150.degree. C. - From 110 to 150.degree. C. took 19 min. - Max. temp. = 150.degree. C.
Spindle: #4

RPM	1.5	3	6	12
Viscosity (cps)	16,000	9,000	7,800	5,700

117 EXAMPLE 47

16% Water (32 grams), 5% Complex (10 grams),
79% Propylene Glycol (158 grams) - Heated to 145-150.degree. C. - From 110 to 150.degree. C. took 19 min. - Max. temp. = 150.degree. C.
Spindle: #3

RPM	6	12	30
Viscosity (cps)	7,220	5,110	3,040

118 EXAMPLE 48

24% Water (48 grams), 5% Complex (10 grams),
71% Propylene Glycol (142 grams) - Heated to 120.degree. C. - From 110 to 125.degree. C. took 19 min. - Max. temp. = 125.degree. C.
Spindle: #2

RPM	30	60
Viscosity (cps)	118.0	108.0

119 EXAMPLE 49

24% Water (48 grams), 5% Complex (10 grams),
71% Propylene Glycol (142 grams) - Heated to 120.degree. C. - From 110 to 125.degree. C. took 19 min. - Max. temp. = 125.degree. C.
Spindle: #4

RPM	1.5	3	6	12
Viscosity (cps)	8,800	6,600	5,000	2,800

120 EXAMPLE 50

24% Water (48 grams), 5% Complex (10 grams),
71% Propylene Glycol (142 grams) - Heated to 120.degree. C. - From

110 to 125.degree. C. took 19 min. - Max. temp. = 125.degree. C.
Spindle: #3

RPM	6	12	30
Viscosity (cps)			
	3,820	2,470	1,100

121 EXAMPLE 51

30% Water (60 grams), 5% Complex (10 grams),
65% Propylene Glycol (130 grams) - Heated to 120.degree. C. - From
110 to 125.degree. C. 19 min. - Max. temp. = 125.degree. C.
Spindle: #2

RPM	12	30	60
Viscosity (cps)			
	692.5	389.0	258.0

122 EXAMPLE 52

30% Water (60 grams), 5% Complex (10 grams),
65% Propylene Glycol (130 grams) - Heated to 120.degree. C. - From
110 to 125.degree. C. 19 min. - Max. temp. = 125.degree. C.
Spindle: #4

RPM	1.5	3	6	12
Viscosity (cps)				
	23,600	11,200	5,400	2,800

123 EXAMPLE 53

30% Water (60 grams), 5% Complex (10 grams),
65% Propylene Glycol (130 grams) - Heated to 120.degree. C. - From
110 to 125.degree. C. 19 min. - Max. temp. = 125.degree. C.
Spindle: #3

RPM	6	12	30
Viscosity (cps)			
	6,100	3,550	2,112

124 EXAMPLES 54

8% Water (16 grams), 5% Complex (10 grams),
87% Methanol (174 grams)
Spindle: #1

RPM	0.3	0.6	1.5
Viscosity (cps)	1,160	960	588

125 EXAMPLE 55

4% Water (8 grams), 10% - 1:4 Complex (20 grams),
86% Propylene Glycol (172 grams)
Spindle: #3

RPM	0.3	0.6
Viscosity (cps)	19,600	18,400

126 EXAMPLE 56

6% Water (12 grams), 10% - 1:4 Complex (20 grams),
84% Propylene Glycol (168 grams)
Spindle: #3

RPM	0.3	0.6
Viscosity (cps)	128,000	67,200

127 EXAMPLE 57

8% Water (16 grams), 10% - 1:4 Complex (20 grams),
82% Propylene Glycol (164 grams)
Spindle: #3

RPM	0.3	0.6
Viscosity (cps)	61,200	56,600

128 EXAMPLE 58

16% Water (32 grams), 10% - 1:4 Complex (20 grams),
74% Propylene Glycol (148 grams)
Spindle: #3

RPM	0.3	0.6
Viscosity (cps)	79,200	49,200

129 EXAMPLE 59

24% Water (48 grams), 10% - 1:4 Complex (20 grams),
66% Propylene Glycol (132 grams)
Spindle: #3

RPM	0.3	0.6
Viscosity (cps)	168,400	89,000

130 EXAMPLE 60

8% Water (16 grams), 5% Complex (10 grams),
87% Methanol (174 grams)
Spindle: #2

RPM	0.3	0.6	1.5
Viscosity (cps)	1,160	960	588

131 EXAMPLE 61

8% Water (16 grams), 5% Complex (10 grams)
87% Methanol (174 grams)
Spindle: #2

RPM	6	12	30
Viscosity (cps)	280	160	80

132 EXAMPLE 62

16% Water (32 grams), 5% Complex (10 grams),
79% Methanol (158 grams)
Spindle: #1

RPM	0.3	0.6	1.5
Viscosity (cps)	9,860	5,940	2,232

133 EXAMPLE 63

16% Water (32 grams), 5% Complex (10 grams),
79% Methanol (158 grams)
Spindle: #2

RPM	6	12	30
Viscosity (cps)			
	665	403	204

134 EXAMPLE 64

20% Water (40 grams), 5% Complex (10 grams), 75% Methanol (150 grams)
Spindle: #1

RPM	0.3	0.6	1.5
Viscosity (cps)			
	13,880	7,460	3,228

135 EXAMPLE 65

20% Water (40 grams), 5% Complex (10 grams), 75% Methanol (150 grams)
Spindle: #2

RPM	6	12	30
Viscosity (cps)			
	905	455	244

136 EXAMPLE 66

27% Water (54 grams), 5% Complex (10 grams), 68% Methanol (136 grams)
Spindle: #2

RPM	0.3	0.6	1.5
Viscosity (cps)			
	17,400	10,250	4,640

137 EXAMPLE 67

27% Water (54 grams), 5% Complex (10 grams) 68% Methanol (136 grams)
Spindle: #2

RPM	6	12	30
Viscosity (cps)			
	1,170	533	271

138 EXAMPLE 68

35% Water (70 grams), 5% Complex (20 grams), 60% Methanol (120 grams) Spindle: #2			
RPM	0.3	0.6	1.5
Viscosity (cps)	16,900	8,900	3,680

139 EXAMPLE 69

35% Water (70 grams), 5% Complex (20 grams), 60% Methanol (120 grams) Spindle: #2			
RPM	6	12	30
Viscosity (cps)	1,175	525	251

140 Propylene glycol and glycerol gels, prepared from a 4:1 weight ratio sodium bentonite clay:PVP intercalates at a 10% by weight intercalate loading, were tested to determine if the gels could hold substantial quantities of hydrophobic silicone oil material in a stable, viscous thixotropic gel (Examples 70-76). It was found that to avoid syneresis (liquid separation) when incorporating both very hydrophobic (silicone oil) and hydrophilic (glycol or glycerol) liquids, a small amount of surfactant, e.g., an amino silane, may be included. The following examples show that viscous gels (of both hydrophobic and hydrophilic liquids) can be prepared without syneresis. The compositions of Examples 70-76 have been stable for six months and remain stable.

141 EXAMPLE 70

27.5%	15% Propylene Glycol Gel w/8% Water
65%	Silicone Oil
0.75%	Abil Surfactant
1.75%	Water
None	Syneresis

142 EXAMPLE 71

27.5%	15% Propylene Glycol Gel w/24% Water
65%	Silicone Oil
0.75%	Abil Surfactant
1.75%	Water

None	Syneresis

143 EXAMPLE 72

27.5%	20% Propylene Glycol Gel w/8% Water
65%	Silicone Oil
0.75%	Abil Surfactant
1.75%	Water
None	Syneresis

144 EXAMPLE 73

37%	10% Glycerol Gel w/0% Water
51%	Silicone Oil
1.0%	Abil Surfactant
11%	Water
None	Syneresis

145 EXAMPLE 74

34%	10% Glycerol Gel w/4% Water
60%	Silicone Oil
1.0%	Abil Surfactant
5%	Water
None	Syneresis

146 EXAMPLE 75

37.5	10% Glycerol Gel w/4% Water
55%	Silicone Oil
1.0%	Abil Surfactant
6.5%	Water
None	Syneresis

147 EXAMPLE 76

37%	10% Glycerol Gel w/4% Water
51%	Silicone Oil
1.0%	Abil Surfactant
11%	Water

None Syneresis

148 The following compositions were prepared to show the viscosity increasing effect of a pH substantially outside of the 6-10, near-neutral range. A composition containing a Na bentonite:PVP complex (4:1 weight ratio clay:PVP) at 7-10% by weight; propylene glycol at 58-66% by weight, and water at 22-26% by weight, with the addition of 5-6% by weight of a 50% active aqueous solution of NaOH to pH 12-13 resulted in a thixotropic gel having a viscosity at 24.degree. C. of 1,500,000 centipoises, without heating. The compositions were prepared by shearing all components except the NaOH in a blender for 3 minutes, then adding the NaOH and shearing for an additional 1 minute. By changing the NaOH to H.sub.2 O ratio to get an optimum pH, an effective hair waving lotion/hair straightener can be obtained at high pH which can be maintained on the hair without running down auto the scalp.

149 Numerous modifications and alternative embodiments of the invention will be apparent to those skilled in the art in view of the foregoing description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the best mode of carrying out the invention. The details of the structure may be varied substantially without departing from the spirit of the invention, and the exclusive use of all modifications which come within the scope of the appended claims is reserved.

CLAIMS:

What is claimed is:

1. A composition comprising exfoliated platelets of an intercalate, together with an organic solvent, said organic solvent present in the composition in an amount in the range of about 10% to about 99.95% by weight of the composition, said exfoliated platelets of said intercalate formed by contacting a layered silicate material, having a moisture content of at least about 4% by weight, with an intercalant polymer having a functionality selected from the group consisting of an aromatic ring; carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester; an SO.sub.x ; a PO.sub.x structure and mixtures thereof, wherein x=2, 3, or 4 to form an intercalating composition, having a weight ratio of polymer to layered material of at least 1:20, to achieve complexing of the polymer between adjacent spaced layers of the layered silicate material from about 8 grams of polymer per 100 grams of the layered silicate material to about 90 grams of polymer per 100 grams of the layered silicate material, without an onium ion or silane coupling agent, to expand the spacing between a predominance of the adjacent platelets of said layered silicate material to at least about 5 .ANG., when measured after sorption of the intercalant polymer and drying to a maximum of 5% by weight water, and exfoliating a predominance of said spaced phyllosilicate platelets.

2. A composition in accordance with claim 1, wherein the concentration of intercalant polymer in said intercalating composition is at least about 0.1% by weight, based on the weight of water and polymer in the intercalating composition.

3. A composition in accordance with claim 2, wherein the concentration of intercalant polymer in said intercalating composition is at least about 1% by weight.

4. A composition in accordance with claim 3, wherein the concentration of intercalant polymer in said intercalating composition is at least about 2% by weight.

5. A composition in accordance with claim 1, wherein the concentration of intercalant polymer in said intercalating composition is in the range of about 10%-60% by weight.

6. A composition in accordance with claim 4, wherein the concentration of intercalant polymer in said intercalating composition is at least about 15% by

weight, based on the dry weight of layered material in the intercalating composition, to achieve spacing of said adjacent platelets of at least about 10 .ANG..

7. A composition in accordance with claim 6, wherein the concentration of intercalant polymer in said intercalating composition is at least about 20% by weight, based on the dry weight of layered material in the intercalating composition.

8. A composition in accordance with claim 7, wherein the concentration of intercalant polymer in said intercalating composition is at least about 30% by weight, based on the dry weight of layered material in the intercalating composition.

9. A composition in accordance with claim 1, wherein the concentration of intercalant polymer in said intercalating composition in the range of about 50% to about 90% by weight, based on the weight of polymer plus water.

10. A composition in accordance with claim 9, wherein the concentration of intercalant polymer in said intercalating composition is in the range of about 50% to about 80% by weight.

11. A composition in accordance with claim 1, wherein the concentration of intercalant polymer in the intercalating composition is at least about 16% by weight, based on the dry weight of the layered material.

12. A composition in accordance with claim 11, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 16% to about 70% by weight, based on the dry weight of the layered material.

13. A composition in accordance with claim 1, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is in the range of about 1:20 to about 10:1.

14. A composition in accordance with claim 11, wherein the weight ratio of intercalant polymer to layered material is at least 1:12.

15. A composition in accordance with claim 14, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is at least 1:5.

16. A composition in accordance with claim 15, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is in the range of 1:5 to 1:3.

17. A composition in accordance with claim 1, wherein the intercalant polymer is selected from the group consisting of polyvinylpyrrolidone; polyvinyl alcohol; polyvinylimine; and mixtures thereof.

18. A composition in accordance with claim 17, wherein the intercalant polymer is polyvinyl alcohol.

19. A composition in accordance with claim 13, wherein the intercalant polymer is polyvinylpyrrolidone.

20. A composition in accordance with claim 18, wherein the intercalant polymer is polyvinyl alcohol having less than about 5% by weight acetal substituents in the polymer.

21. A composition in accordance with claim 17, wherein the intercalant polymer has a weight average molecular weight in the range of about 100 to about 100,000.

22. A composition in accordance with claim 17, wherein the intercalant polymer has a weight average molecular weight in the range of about 200 to about 40,000.

23. A composition in accordance with claim 22, wherein the intercalant polymer is polyvinylpyrrolidone.

24. A composition in accordance with claim 22, wherein the intercalant polymer is a polyvinyl alcohol.

25. A composition in accordance with claim 1, wherein the intercalant polymer is a homopolymer or copolymer of N-vinylpyrrolidone.

26. A method of increasing the viscosity of an organic liquid by combining said organic liquid with about 0.05% to about 60% by weight of the composition of exfoliated platelets of an intercalate complex of a phyllosilicate having adjacent phyllosilicate platelets and an intercalant polymer comprising:

contacting the phyllosilicate, having a water content of at least about 4% by weight, with said intercalant polymer having a functionality selected from the group consisting of an aromatic ring; carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester; an SO.sub.x ; a PO.sub.x structure and mixtures thereof, wherein x=2, 3, or 4, to form an intercalating composition having a weight ratio of intercalant polymer to phyllosilicate of at least 1:20, to form an intercalate, having about 8 grams of polymer per 100 grams of phyllosilicate to about 90 grams of polymer per 100 grams of phyllosilicate, without an onium ion or silane coupling agent, wherein intercalation of said polymer between said adjacent phyllosilicate platelets of said phyllosilicate is sufficient to space said adjacent phyllosilicate platelets a distance of at least about 5 .ANG.;

exfoliating a predominance of said spaced phyllosilicate platelets; and

combining said exfoliated platelets with said organic liquid.

27. The method of claim 26, wherein said intercalating composition includes a water intercalating carrier comprising about 4% to about 5000% by weight water, capable of dissolving said polymer, based on the dry weight of said phyllosilicate.

28. The method of claim 27, wherein said intercalating composition includes water in an amount of about 30% to about 40% by weight.

29. The method of claim 28, wherein said water content of said intercalating composition comprises about 35% to about 40% by weight, based on the dry weight of said phyllosilicate.

30. The method of claim 27, wherein said intercalating composition comprises about 5% to about 50% by weight water, based on the dry weight of said phyllosilicate.

31. The method of claim 27, wherein said intercalating composition includes water in an amount of about 7% to about 100% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

32. A composition comprising an organic liquid selected from the group consisting of monohydric alcohols, polyhydric alcohols and mixtures thereof, in an amount of about 40% to about 99.95% by weight of the composition and about 0.05% to about 60% by weight of the composition of exfoliated platelets of an intercalate of a phyllosilicate material having adjacent spaced platelet surfaces, said exfoliated platelets formed by contacting said phyllosilicate material, having a water content of at least about 4% by weight, with an intercalant polymer having a functionality selected from the group consisting of an aromatic ring; carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester; an SO.sub.x ; a PO.sub.x structure and mixtures thereof, wherein x=2, 3, or 4, said polymer contacting said phyllosilicate material in an intercalating composition having a concentration of about 16% to about 90% polymer, based on the dry weight of said phyllosilicate material, to form said intercalate having said intercalant polymer sorbed between said adjacent spaced platelet surfaces of the phyllosilicate material and complexed on said platelet surfaces of said phyllosilicate material in a weight ratio of polymer to phyllosilicate material of 8 grams of polymer per 100 grams of

phyllosilicate material to 90 grams of polymer per 100 grams of phyllosilicate material, without an onium ion or silane coupling agent, to expand the spacing between a predominance of the adjacent phyllosilicate platelet surfaces to at least about 5 .ANG., when measured after sorption of the polymer and drying of the intercalate to a maximum water content of 5% by weight, and exfoliating a predominance of said spaced phyllosilicate platelets.

33. The composition of claim 32, wherein the intercalate is exfoliated into a predominance of single platelets having said intercalant polymer complexed onto said platelet surfaces.

34. The composition of claim 32, wherein the alcohol is a monohydric alcohol having 1 to about 5 carbon atoms.

35. The composition of claim 32, wherein the alcohol is a polyhydric alcohol selected from the group consisting of glycols, glycerols, and mixtures thereof.

36. A composition in accordance with claim 32, wherein the intercalant composition has a weight ratio of intercalant polymer to phyllosilicate of at least about 1:20.

37. A composition in accordance with claim 36, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is at least about 1:12.

38. A composition in accordance with claim 37, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is at least about 1:10.

39. A composition in accordance with claim 38, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition is at least about 1:5.

40. A composition in accordance with claim 39, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition in the range of about 1:5 to about 9:1.

41. A composition in accordance with claim 40, wherein the weight ratio of intercalant polymer to phyllosilicate in said intercalating composition in the range of about 1:5 to about 1:3.

42. A composition in accordance with claim 36, wherein the concentration of intercalant polymer in the intercalating composition is at least about 16% by weight, based on the dry weight of the phyllosilicate.

43. A composition in accordance with claim 42, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 16% to about 70% by weight, based on the dry weight of the phyllosilicate.

44. A composition in accordance with claim 42, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 16% to less than about 35% by weight, based on the dry weight of the phyllosilicate.

45. A composition in accordance with claim 43, wherein the concentration of intercalant polymer in the intercalating composition is in the range of about 35% to less than about 55% by weight, based on the dry weight of the phyllosilicate.

46. A composition in accordance with claim 43, wherein the concentration of the intercalant polymer in the intercalating composition is in the range of about 55% to less than about 70% by weight, based on the dry weight of the phyllosilicate.

47. A composition in accordance with claim 32, wherein the organic liquid is selected from the group consisting of alcohols, ketones, aldehydes, esters, glycols, glycerols, or ethers and mixtures thereof.

48. A method of manufacturing a composition containing about 10% to about 99.95% by weight of an organic liquid and about 0.05% to about 60% by weight of exfoliated platelets of an intercalated layered material, said intercalated layered material having a water-soluble polymer intercalated between and bonded to adjacent platelet surfaces thereof through a bonding mechanism selected from the group consisting of ionic complexing; electrostatic complexing; chelation; hydrogen bonding; dipole/dipole; Van Der Walls forces; and any combination thereof, comprising:

contacting the layered material with a water-soluble intercalant polymer having a functionality selected from the group consisting of an aromatic ring; carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester; an SO.sub.x ; a PO.sub.x structure and mixtures thereof, wherein x=2, 3, or 4 and water to form an intercalating composition, thereby forming an intercalate having said polymer intercalated between said adjacent platelets, without an onium ion or silane coupling agent, in an amount sufficient to space said adjacent platelets a distance of at least about 5 .ANG.;

combining the intercalate with said organic liquid; and

exfoliating the spaced platelets of said intercalate into predominantly individual platelets.

49. The method of claim 48, wherein said layered material is a phyllosilicate and said intercalating composition is an aqueous solution comprising about 4% to about 5000% by weight water, based on the dry weight of said phyllosilicate in said intercalating composition.

50. The method of claim 49, wherein said intercalating composition comprises about 30% to about 50% water, based on the dry weight of the phyllosilicate.

51. The method of claim 50, wherein said intercalating composition comprises about 35% to about 45% by weight water.

52. A method of manufacturing a composition comprising an organic liquid and exfoliated platelets of a phyllosilicate intercalate comprising:

contacting the phyllosilicate having adjacent spaced phyllosilicate platelets with a water-soluble intercalant polymer having a functionality selected from the group consisting of an aromatic ring; carbonyl; carboxyl; hydroxyl; amine; amide; ether; ester; an SO.sub.x ; a PO.sub.x structure and mixtures thereof, wherein x=2, 3, or 4 and water, wherein the weight ratio of the intercalant polymer to phyllosilicate is at least 1 to about 20, and the concentration of said water-soluble intercalant polymer is at least about 5% up to about 900% polymer, based on the dry weight of the phyllosilicate, to form said phyllosilicate intercalate having said intercalant polymer intercalated between said adjacent phyllosilicate platelets, without an onium ion or silane coupling agent, and in an amount sufficient to space said adjacent phyllosilicate platelets to a distance of at least about 5 .ANG.;

combining the intercalate with said organic liquid; and

exfoliating a predominance of the spaced phyllosilicate platelets.

53. A composition in accordance with claim 1, wherein the weight ratio of polymer to layered silicate material complexed between adjacent spaced layers of the layered silicate material is from about 16 grams of polymer per 100 grams of layered silicate material to about 90 grams of polymer per 100 grams of layered silicate material.

54. A composition in accordance with claim 53, wherein the layered silicate material is selected from the group consisting of montmorillonite; nontronite; beidellite; volksonite; hectorite; saponite; sauconite; sobockite; stevensite; svinfordite; vermiculite; illite; rectorite; tarosovite; ledikite; and mixtures thereof.

55. A composition in accordance with claim 53, wherein the weight ratio of polymer to layered silicate material complexed between adjacent spaced layers of the layered silicate material is from about 16 grams of polymer per 100 grams of layered silicate material to about 80 grams of polymer per 100 grams of layered silicate material.

56. A composition in accordance with claim 55, wherein the weight ratio of polymer to layered silicate material complexed between adjacent spaced layers of the layered silicate material is from about 20 grams of polymer per 100 grams of layered silicate material to about 60 grams of polymer per 100 grams of layered silicate material.

57. A composition in accordance with claim 14, wherein the weight ratio of intercalant polymer to layered silicate material in the intercalating composition is in the range of 1:20 to 1:3.

58. A composition in accordance with claim 6, wherein the concentration of intercalant polymer in said intercalating composition is about 15% to about 90% by weight, based on the dry weight of the layered silicate material in the intercalating composition.

59. A composition in accordance with claim 11, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 90% by weight, based on the dry weight of the layered silicate material in the intercalating composition.

60. A composition in accordance with claim 59, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 80% by weight, based on the dry weight of the layered silicate material in the intercalating composition.

61. A method in accordance with claim 26, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 10 grams of polymer per 100 grams of phyllosilicate to about 90 grams of polymer per 100 grams of phyllosilicate.

62. A method in accordance with claim 61, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 16 grams of polymer per 100 grams of phyllosilicate to about 90 grams of polymer per 100 grams of phyllosilicate.

63. A method in accordance with claim 62, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 16 grams of polymer per 100 grams of phyllosilicate to about 80 grams of polymer per 100 grams of phyllosilicate.

64. A method in accordance with claim 63, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 20 grams of polymer per 100 grams of phyllosilicate to about 60 grams of polymer per 100 grams of phyllosilicate.

65. A method in accordance with claim 26, wherein the weight ratio of intercalant polymer to phyllosilicate in the intercalating composition is in the range of 1:20 to 1:3.

66. A method in accordance with claim 26, wherein the concentration of intercalant polymer in said intercalating composition is about 15% to about 90% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

67. A method in accordance with claim 66, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 90% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

68. A method in accordance with claim 67, wherein the concentration of intercalant

polymer in said intercalating composition is about 16% to about 80% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

69. A composition in accordance with claim 32, wherein the weight ratio of polymer to phyllosilicate material complexed between adjacent spaced layers of the phyllosilicate material is from about 10 grams of polymer per 100 grams of phyllosilicate material to about 90 grams of polymer per 100 grams of phyllosilicate material.

70. A composition in accordance with claim 69, wherein the weight ratio of polymer to phyllosilicate material complexed between adjacent spaced layers of the phyllosilicate material is from about 16 grams of polymer per 100 grams of phyllosilicate material to about 90 grams of polymer per 100 grams of phyllosilicate material.

71. A composition in accordance with claim 70, wherein the weight ratio of polymer to phyllosilicate material complexed between adjacent spaced layers of the phyllosilicate material is from about 16 grams of polymer per 100 grams of phyllosilicate material to about 80 grams of polymer per 100 grams of phyllosilicate material.

72. A composition in accordance with claim 71, wherein the weight ratio of polymer to phyllosilicate material complexed between adjacent spaced layers of the phyllosilicate material is from about 20 grams of polymer per 100 grams of phyllosilicate material to about 60 grams of polymer per 100 grams of phyllosilicate material.

73. A composition in accordance with claim 36, wherein the weight ratio of intercalant polymer to phyllosilicate material in the intercalating composition is in the range of 1:20 to 1:3.

74. A composition in accordance with claim 32, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 80% by weight, based on the dry weight of the phyllosilicate material in the intercalating composition.

75. A method in accordance with claim 48, wherein the weight ratio of polymer to layered material complexed between adjacent spaced layers of the layered silicate material is from about 8 grams of polymer per 100 grams of layered silicate material to about 90 grams of polymer per 100 grams of layered silicate material.

76. A method in accordance with claim 75, wherein the weight ratio of polymer to layered material complexed between adjacent spaced layers of the layered silicate material is from about 10 grams of polymer per 100 grams of layered silicate material to about 90 grams of polymer per 100 grams of layered silicate material.

77. A method in accordance with claim 76, wherein the weight ratio of polymer to layered material complexed between adjacent spaced layers of the layered silicate material is from about 16 grams of polymer per 100 grams of layered silicate material to about 80 grams of polymer per 100 grams of layered silicate material.

78. A method in accordance with claim 77, wherein the weight ratio of polymer to layered material complexed between adjacent spaced layers of the layered silicate material is from about 20 grams of polymer per 100 grams of layered silicate material to about 60 grams of polymer per 100 grams of layered silicate material.

79. A method in accordance with claim 48, wherein the weight ratio of intercalant polymer to layered material in the intercalating composition is in the range of 1:20 to 1:3.

80. A method in accordance with claim 48, wherein the concentration of intercalant polymer in said intercalating composition is about 15% to about 90% by weight, based on the dry weight of the layered material in the intercalating composition.

81. A method in accordance with claim 80, wherein the concentration of intercalant

polymer in said intercalating composition is about 16% to about 90% by weight, based on the dry weight of the layered material in the intercalating composition.

82. A method in accordance with claim 81, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 80% by weight, based on the dry weight of the layered material in the intercalating composition.

83. A method in accordance with claim 52, wherein the weight ratio of polymer to layered material complexed between adjacent spaced layers of the phyllosilicate is from about 8 grams of polymer per 100 grams of phyllosilicate to about 90 grams of polymer per 100 grams of phyllosilicate.

84. A method in accordance with claim 83, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 16 grams of polymer per 100 grams of phyllosilicate to about 90 grams of polymer per 100 grams of phyllosilicate.

85. A method in accordance with claim 84, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 16 grams of polymer per 100 grams of phyllosilicate to about 80 grams of polymer per 100 grams of phyllosilicate.

86. A method in accordance with claim 85, wherein the weight ratio of polymer to phyllosilicate complexed between adjacent spaced layers of the phyllosilicate is from about 20 grams of polymer per 100 grams of phyllosilicate to about 60 grams of polymer per 100 grams of phyllosilicate.

87. A method in accordance with claim 52, wherein the weight ratio of intercalant polymer to phyllosilicate in the intercalating composition is in the range of 1:20 to 1:3.

88. A method in accordance with claim 52, wherein the concentration of intercalant polymer in said intercalating composition is about 15% to about 90% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

89. A method in accordance with claim 88, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 90% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

90. A method in accordance with claim 89, wherein the concentration of intercalant polymer in said intercalating composition is about 16% to about 80% by weight, based on the dry weight of the phyllosilicate in the intercalating composition.

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DOCUMENT-IDENTIFIER: US 4740488 A

TITLE: Modified clay sorbents

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PRIOR-ART-DISCLOSED:

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Search Selected | Search ALL

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ART-UNIT: 116

PRIMARY-EXAMINER: Dees; Carl F.

ATTY-AGENT-FIRM: Rohm & Monsanto

ABSTRACT:

Modified clay is a general purpose sorbent for the removal of trace organic pollutants from process effluent streams. An expandible smectite clay, such as montmorillonite, is placed in an aqueous suspension to expand the layers. The expanded clay is then treated with an excess of a solution of hydroxy-aluminum, in particular, a hydroxy-aluminum solution having an OH.sup.- /Al ratio of about 2.54 and a pH in the vicinity of 4.5. The weight of clay to volume of hydroxy-aluminum solution may vary from about 1:10 and 1:25. The treated clay is filtered, washed, dried, and powdered by techniques well known in the art, and then the entire treatment sequence is repeated. The modified, powdered clay removes organic pollutants from industrial effluent in the ppb-ppq range. In particular, the modified clay is useful in removing traces of PCBs and Dioxin.

9 Claims, 0 Drawing figures
Exemplary Claim Number: 9

BRIEF SUMMARY:

1 BACKGROUND OF THE INVENTION

2 This invention relates generally to systems for removing trace pollutants from industrial effluent streams, such as by a sorbent, and more particularly, to a system for removal of such trace pollutants using a modified clay as the sorbent.

3 There is a clear, generally known need to reduce the level of pollution in the aquatic environment. A significant first step in effecting reduction of the level of such pollution would be achieved by removing trace organic contaminants, such as polychlorinated biphenyls (PCBs), polychlorinated dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). Such trace organic contaminants are found in industrial effluent water as undesirable by-products of chemical manufacturing. For example, 2,3,7,8-Tetrachlorodioxin (2,3,7,8-TCDD) is formed during the production of 2,4,5-Trichlorophenol, which is an ingredient of many pesticides. Even at extremely low concentrations, 2,3,7,8-TCDD is the most toxic isomer of dioxin and is generally referred to as "Dioxin."

4 A known, highly advantageous technique for removing trace amounts of organic pollutants in very large volumes of waste water, utilizes a sorbent to which the contaminant is adsorbed. The most commonly used adsorbant today is activated carbon, the production of which utilizes a wide variety of carbonaceous starting materials, such as anthracite and bituminous coal, carbonized shells, peat, etc. The various known methods of activating charcoal can be grouped into two categories. The first category includes chemical activation wherein the carbonaceous materials are impregnated with an activating agent and then pyrolyzed. The second category comprises heat treatment processes wherein chars are heated to temperatures between 350.degree. and 1000.degree. C. in the presence of CO.sub.2, N.sub.2, O.sub.2, HCl, Cl.sub.2, H.sub.2 O and other gases. A portion of the char is burned as the surface area and "activity" of the carbon increases. Modern manufacturing techniques, which include careful monitoring of the activation parameters, yield activated products having high surface areas in a wide range of uniform particle sizes.

5 In addition to activated charcoal, natural soils and sediments containing various amounts of bound organic carbon or synthetic "zeolite-like" sorbents with specific affinity for rigid, planar aromatic molecules like dioxin have been considered. One known synthetic sorbent is described in U.S. Pat. No. 4,040,990. All of the known systems have significant problems which render them substantially less than ideal for the purpose of removing trace organics from large quantities of water. Activated charcoal and synthetic sorbents are very expensive and therefore do not provide an economical solution to the problem. Natural soils and sediments, however, are less expensive than the activated charcoal and synthetic sorbents, but are not uniform, and in fact exhibit too much variation in binding affinity to be used in large scale technology.

6 In addition to the systems discussed hereinabove for the disposal of organic pollutants, such as Dioxin, a variety of other methods are known. These include: photolytic dechlorination, microbial degradation, and thermal decomposition. Photolytic dechlorination has been used to detoxify Dioxin-contaminated soil, as well as Dioxin admixed with asphalt and heavy oil. In such situations, the initial concentration of Dioxin was many orders of magnitude higher than is usually present in industrial waste water. For example, the concentration of Dioxin in the contaminated soil, the asphalt, and heavy oil, was in the ppm range, while the concentration in industrial waste water is typically in the ppq range. The process of photolytic dechlorination is disadvantageously characterized by a requirement of high absorption of light photons, and therefore is practical only when high initial concentration of the pollutants is present, and the samples can readily be exposed to light.

7 As is the case with photolytic dechlorination, the process of microbial degradation also requires the pollutant to be present in high concentration. However, no microorganism has yet been developed which is capable of degrading

Dioxin. The process of thermal decomposition requires operating temperatures in excess of 1000.degree. C., and the technology required to implement this process is still in a developmental stage. It is a problem with all three of these processes that they are ineffective when the polluting compound is present in water at extremely low concentrations, illustratively on the order of pptr to ppq.

8 Swelling clays, generically designated as smectites, have been used widely in the prior art as catalysts, catalyst supports, molecular sieves, adsorbers, and absorbers. The utility of these clays for these purposes is derived from the physical properties of the clay itself. Smectites, such as montmorillonite, have a layered lattice structure in which two-dimensional oxyanions are separated by layers of hydrated cations. The layered structure enable intercalation of layers of a different character between the sheets of the clay structure. In addition, "pillared" clays have been developed wherein intercalated thermally stable cations act as props, or pillars, to support the silicate layers of the clay in the absence of a swelling solvent. The pillar size, or spacing, and hence, the pore size of the clays can be adjusted so as to permit the making of suitable catalysts, catalyst supports, molecular sieves, etc., for various purposes, particularly in the petroleum processing field.

9 A variety of expanded layer smectite clays, which are based on various cationic species, have been disclosed in the prior art. These include Al, Ti, Fe, Cr, Ni, and Zr. Examples of such clays are described in U.S. Pat. Nos. 4,060,480; 4,176,090, and 4,216,188. The use of inorganic exchange ions to expand smectite layers is described in U.S. Pat. No. 4,060,480. As described in this reference, the clay is treated with hydroxy-aluminum polymers or oligomers in solution, and subsequently the clay is dried and calcined to produce supporting pillars between clay layers. Such pillars serve to maintain the expanded layer state in the clay and leave pores having a rectangular opening configuration, framed by the pillars and the clay layers.

10 None of the substrates described in the references cited herein are known to be used as compositions which perform as a sorbent for industrial pollutants in an effluent stream. It is to be remembered that the term "adsorption" generally refers to a first step in catalysis and may not necessarily be applicable to the mechanism of a process for removing pollutants from industrial effluents. As is known, a catalyst will adsorb and release. Effluent treatment, however, requires that the composition adsorb the pollutant and retain same.

11 It is, therefore, an object of this invention to produce an inexpensive system for removing trace organic contaminants which pollute an aquatic environment.

12 It is also an object of this invention to provide a process for removing trace organic pollutants, typically on the order of between pptr and ppq.

13 It is another object of this invention to provide a system for removing contaminants from an industrial waste water stream, the contaminants including dioxin, PCBs, PPCDs, and PCDDs.

14 It is a further object of this invention to provide a material having high sorptive capacity and binding affinity for organic pollutants.

15 It is still another object of this invention to provide a sorbent material which is inexpensive to use, due to, inter alia, low cost starting materials and high sorptive capacity requiring the use of small quantities of sorbent.

16 It is yet another object of this invention to provide a process for removing trace organic contaminants which is simple and inexpensive to implement.

17 It is still a further object of this invention to provide a system for removing trace amounts of contaminants which can be used simply and with existing technology.

18 It is a still further object of this invention to provide a sorbent material which can easily, and safely, be disposed of after it has been used to remove trace

organic pollutants.

19 SUMMARY OF THE INVENTION

20 The foregoing and other objects are achieved by this invention which provides a pillared clay composition which is formed by a process including the steps of swelling an expandible clay with a solvent, contacting the swollen clay with an aqueous solution of hydroxy-aluminum, and filtering the mixture thus formed to produce a filter cake. The filter cake is then dried and powdered. After such powdering, the filter cake product is once again subjected to an aqueous solution of hydroxy-aluminum, filtered to produce a further filter cake, dried, and powdered.

21 In one embodiment of the invention, the expandible clay is a smectite clay, and preferably, montmorillonite. Additionally, the solvent which is used to swell the expandible clay is water.

22 Preferably, the aqueous solution of hydroxy-aluminum should have an OH.sup.- /Al ratio of approximately between 2.0 to 3.1, and preferably approximately 2.54. Additionally, the aqueous solution has a pH in the range of approximately between 3.6 to 5.4, and preferably approximately 4.5.

23 In accordance with a method aspect of the invention, an expandible clay, illustratively a smectite clay such as montmorillonite is caused to swell. The swollen montmorillonite is subjected to an aqueous solution of hydroxy-aluminum having an OH.sup.- /Al ratio of approximately 2.54 and a pH of approximately 4.5. The resulting mixture is filtered to produce a filter cake and washed. The filter cake is then dried and powdered, and once again subjected to an aqueous solution of hydroxy-aluminum. The steps of filtering the mixture to form a filter cake, washing the filter cake, drying the filter cake, and powdering the filter cake are all repeated.

24 In accordance with a use aspect of the invention, the pillared clay composition which is formed in accordance with the foregoing method is applied to remove organic trace components from industrial effluents. Removal of the trace organic pollutants in the industrial waste effluent is effected by microseparation of the trace pollutants from water.

DETAILED DESCRIPTION:

1 DETAILED DESCRIPTION OF THE INVENTION

2 In accordance with the invention, a clay is modified to have an advantageously high sorptive capacity and binding affinity for organic pollutants in water. Clay is particularly suited to the task of treating polluted and contaminated effluents because it is chemically homogeneous, plentiful, and inexpensive. The invention effects a simple, easy to implement modification to the clay. In the practice of the invention, an expandible clay is subjected to a solvent, such as water, so that it swells and the swollen clay is then treated with a polymeric solution of a metal hydroxide, such as hydroxy-aluminum.

3 In a preferred embodiment of the invention, montmorillonite clay is swollen with distilled water, dried, and treated with an excess of hydroxy-aluminum. Preferably the hydroxy-aluminum solution is 0.3M in water. The exact composition of the hydroxy-aluminum is difficult to determine, however, use of a commercially available solution of hydroxy-aluminum ensures that the solution is preferably "aged", thereby assuring that polymeric hydroxy-aluminum will be available. The ratio of OH.sup.- /Al is preferably in the range of approximately between 2.0 and 3.1. In a specific illustrative embodiment of the invention, a commercially available solution of hydroxy-aluminum (Reheis Co.) has been utilized with advantageous results. This known solution has a OH.sup.- /Al ratio of 2.54 and a pH of 4.5. The stock solution is available in a 6M concentration which can be suitably diluted with water to obtain the desired concentration.

4 The smectite clay used in the practice of the invention is advantageously selected to be sodium montmorillonite, which possesses a charge density in the range of 0.8 to 1.1 meq/g smectite. However, any other swelling form of montmorillonite, such as lithium or potassium montmorillonite, can be used in the practice of the invention. Other smectite clays, such as hectorites, beidellites, nontronites, saponites, etc. can be utilized in the production of a modified clay in accordance with the principles of the invention hereof. In a specific illustrative embodiment, Na-montmorillonite (Wyoming SWY-1) obtained from Source Clay Minerals Repository, University of Missouri, Columbia, MO was utilized.

5 The cross-linking, or pillaring, agent used in this invention is a metal hydroxide, specifically hydroxy-aluminum. The metal component, however, could be chromium or some other metal. Hydroxy aluminum is a polynuclear cation formed according to the following reaction:

6 Al(OH).sub.2.sup.+1 .fwdarw.Al.sub.6 (OH).sub.12.sup.+6

6 Due to its positive charge, the hydroxy-aluminum cation-exchanges on the negatively charged clay surface. Due to its polymeric size, the hydroxy-aluminum cation is virtually nonexchangeable in conditions of low ionic strength and pHs between 2 and 11. As shown by FTIR studies of the composition produced in accordance with the invention, these positively charged polynuclear cations bind strongly to the interlayer and external surfaces of the clay; the nonexchangeability rendering the kind of stability required for a sorbent in an aqueous environment.

7 It is difficult to ascertain whether all exchangeable cations are displaced by hydroxy-aluminum, however, the preparatory techniques to be described hereinbelow strive for complete exchange. Pre-swollen clay is subjected to a hydroxy-aluminum solution twice, which solution is greatly in excess of the stoichiometric amount (as high as a 30-fold excess in the illustrative example given hereinbelow).

8 Altering the OH.sup.- /Al ratio may have some effect on the binding capacity of the modified clay with respect to specific pollutants. The OH.sup.- /Al ratio can be varied in the range of about 2.0 to 3.1, and is preferably 2.54. Lowering the OH.sup.- /Al ratio tends to reduce the size of the polymers formed, thereby leading to a reduction in the crosslinking height. Increasing the OH.sup.- /Al ratio results in Gibbsite formation which tends to precipitate in the spaces between clay crystallites and the interlayer spacing. Gibbsite precipitation may lower the macroporosity of the sorbent.

9 In a method aspect of the invention, the general procedure for producing a modified clay sorbent for removal of trace pollutants in waste effluent water is as follows:

10 (1) An expandible-type clay is swollen with a solvent. In a particularly advantageous embodiment of the invention, water is used for this purpose because it is the only inexpensive solvent having a solvation energy which can overcome the combination of Van der Waal's attraction between the clay layers and the electrostatic forces provided by the interlayer exchangeable cations, both of which oppose interlayer expansion. The clay:water ratio is not important since smectites expand to almost infinite interlayer separation as long as the volume of water is large enough to produce such separation. In a specific embodiment, a 1:100 ratio of clay to water is used. Following expansion, the clay is sedimented, illustratively by centrifugation, and the supernatant water is removed by suction prior to the addition of hydroxy-aluminum in the next step.

11 (2) The swollen clay is contacted with an aqueous solution of hydroxy-aluminum. The ratio of clay weight to volume of hydroxy-aluminum solution is in the range of 1:10 to 1:25. Thus, the solution contains an excess of hydroxy-aluminum. In a specific illustrative embodiment, a 0.3M solution of hydroxy-aluminum having an OH.sup.- /Al ratio of 2.54 and a pH of 4.5 produced advantageous results. This solution was approximately 5% by weight (50 mg/ml) expanded clay. Higher clay concentration reduces interlayer expansion and the lateral movement of individual

clay layers, thereby producing a "zeolite-like" micropore structure.

12 (3) Next, the modified clay is filtered by any known technique to produce a filter cake which is subsequently washed and dried, illustratively in a 60.degree. C. oven for a couple of days or in a 110.degree. C. oven overnight. The dried filter cake is then ground into a powder by any known means, such as by a water-cooled powder grinder.

13 (4) The powdered, clay product produced thus far is then resubjected to the hydroxy-aluminum treatment, filtered, dried, and powdered again.

14 The modified clay product produced by the abovedescribed process is effective to remove trace pollutants from an aqueous environment in concentrations as low as pptr to ppq. These trace pollutants include, inter alia, polychlorinated biphenyls, polychlorinated dioxin, polychlorinated dibenzofurans, octachlorodioxin, hexachlorobiphenyl, and 2,3,7,8-tetrachlorodioxin.

15 The binding affinity or the linear partition coefficient (PC) of a sorbent for a given organic compound in solution is defined as the ratio between the surface concentration of the compound and its solution concentration. The higher the value of PC, the smaller the amount of sorbent required to attain a predetermined level of pollutant removal and the cheaper the overall process is. A value of at least 10,000 is preferable for sorbent PC for effective and efficient operation of sorption technology in pollutant removal from industrial effluent water.

16 Examples of high binding affinity for octachlorodioxin OCDD) as a surrogate of polychlorinated dioxins, and hexachlorobiphenyl (HCB) as a representative of polychlorinated biphenyls, are given hereinbelow as proof that the modified clay is a general purpose sorbent for the removal of trace organic pollutants from process effluent streams.

17 EXAMPLE 1

18 Modified clay was manufactured in accordance with the specific illustrative embodiment described hereinabove. A 0.28 mg/ml suspension of the modified clay was mixed with filtered, distilled water. Radiolabeled OCDD was injected under the water and the mixture was agitated for 24 hours. A small amount of Tetrahydrofuran (THF), an organic solvent which is miscible in water, was added to maintain OCDD in soluble form. From the amount of OCDD bound to the modified clay and the amount of OCDD found in solution, a PC of 80,000 was observed.

19 EXAMPLE 2

20 The same experimental conditions as described above in Example 1 were repeated using natural montmorillonite as a sorbent. A PC value of 1,500 was observed.

21 EXAMPLE 3

22 The experiment of example 1 was performed using HCB in place of OCDD. Since HCB is more soluble in water, THF was not added to the system. The modified clay was observed to have a PC value of 25,000.

23 In a practical embodiment of the invention, an effective amount of the modified product produced by the inventive method can be stirred into a settling tank into which industrial effluent water is pumped. Following absorption of pollutants, the supernatant liquid, largely devoid of contaminants, can be separated from the sorbent by flocculation or settling. In an alternative embodiment, the effluent water can be continuously pumped through a series of stirred reactors containing the modified clay such that the outlet water will be stripped of pollutants. The used sorbent can be disposed of as a solid environmental waste, or be regenerated.

24 Although the invention has been described in terms of specific embodiments and applications, persons skilled in the art can, in light of this teaching, generate additional embodiments without exceeding the scope or departing from the spirit of the claimed invention. Accordingly, it is to be understood that the descriptions

in this disclosure are proffered to facilitate comprehension of the invention and should not be construed to limit the scope thereof.

CLAIMS:

What is claimed is:

1. A pillared clay composition formed by a process comprising the steps of:

swelling an expandible clay with a solvent;

contacting the swollen clay with an aqueous solution of hydroxy-aluminum to produce a mixture;

filtering said mixture to produce a filter cake;

drying said filter cake;

powdering said filter cake; and

repeating said steps of contacting, filtering, drying, and powdering.

2. The pillared clay composition of claim 1 wherein said expandible clay is a smectite.

3. The pillared clay composition of claim 2 wherein said smectite is montmorillonite.

4. The pillared clay composition of claim 1 wherein said solvent is water.

5. The pillared clay composition of claim 1 wherein said aqueous solution of hydroxy-aluminum has an OH.sup.- /Al ratio of approximately between 2.0 to 3.1.

6. The pillared clay composition of claim 5 wherein said OH.sup.- /Al ratio is approximately 2.54.

7. The pillared clay composition of claim 5 wherein said aqueous solution has a pH in the range of approximately between 3.6 and 5.4.

8. The pillared clay composition of claim 7 wherein said pH is approximately 4.5.

9. A method of preparing a composition for removing organic trace components from industrial effluents, the method comprising:

forming a swollen montmorillonite;

contacting said swollen montmorillonite with an aqueous solution of hydroxy-aluminum, said solution having an OH.sup.- /Al ratio of approximately 2.54 and a pH of approximately 4.5 to produce a mixture;

filtering said mixture to produce a filter cake;

washing said filter cake;

drying said filter cake;

powdering said filter cake; and

repeating said steps of forming, contacting, filtering, washing, drying, and powdering.